PB-231 250

PHYSICAL-CHEMICAL TREATMENT OF RAW MUNICIPAL WASTEWATER

Dolloff F. Bishop, et al

District of Columbia Department of Environmental Services
Washington, D.C.

December 1973

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PB 231 250

SELECTED WATER RESOURCES ABSTRACTS
INPUT TRANSACTION FORM

3. Accession No. W 74-06509

4. Title

PHYSICAL-CHEMICAL TREATMENT OF RAW MUNICIPAL WASTEWATER,

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9. Organization

EPA-DC Pilot Plant
5000 Overlook Avenue S.W.
Washington, D.C. 20032

10. Project No. EPA Project 11010 EYM

11. Contract/Grant No. 14-12-818

15. Supplementary Notes

Environmental Protection Agency, Technology Series Report Number EPA-670/2-73-070, September 1973. 60p, 13 fig, 16 tab, 30 ref.

16. Abstract Physical-chemical treatment of raw wastewater consisted of two-stage lime clarification with intermediate recarbonation, filtration, pH control, ion exchange or breakpoint chlorination, and carbon adsorption. Lime treatment with approximately 300 mg/l of CaO increased the wastewater pH to 11.5 and removed 96% of the phosphorus and 80% of the organics. In the second stage, recarbonation with 120 mg/l of CO_2 and mineral addition of 5 mg/l of Fe^{+++} reduced the pH to 10.0 and precipitated excess Ca^{++} as $CaCO_3$. Dual media filtration decreased effluent suspended solids and total phosphorus to less than 5 mg/l and 0.15 mg/l as P, respectively. Addition of 10 mg/l chlorine to the filter influent controlled biological growth within the filter and produced filter runs of greater than 50 hours. With extensive operator surveillance, the clinoptilolite exchange media reduced the NH_3 to less than 1 mg/l as NH_4^+-N. Breakpoint chlorination oxidized the NH_3 to N_2, leaving a residual NH_3-N concentration of less than 0.4 mg/l. The 20 mg/l of soluble BOD entering the granular carbon columns produced anaerobic biological growth on the carbon, which contributed to heavy H_2S production and high carbon losses during backwash. Breakpoint chlorination ahead of carbon adsorption minimized biological activity.

The complete physical-chemical system, with ion exchange, removed 98% of the phosphorus, 95% of the organics (COD) and 78% of the total nitrogen. With breakpoint chlorination, the complete system removed 98% of the phosphorus, 94% of the organics (COD) and 86% of the total nitrogen. (Kisenbauer - EPA)

17a. Descriptors

*Wastewater Treatment, *District of Columbia, Biochemical Oxygen Demand, *Flocculation, Anaerobic Conditions, Calcium Carbonate, Phosphorus, *Filtration, Chemical Oxygen Demand, Nitrogen, *Adsorption, Colloids, Lime, *Ion Exchange, Ammonia, Organic loading, Sedimentation,

17b. Identifiers

*Physical-Chemical Treatment, ~~Organic Loading~~ Lime Clarification, *Municipal wastewater, Carbon Adsorption, Breakpoint Chlorination, Recarbonation, ~~Combined treatment~~

17c. COWRR Field & Group 05D

Copy Available from GPO Sup Doc as EP1.23:670/2-73-070, $1.05; microfiche from NTIS as PB-231 250 $1.45

18. Availability

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EPA-670/2-73-070
September 1973

PHYSICAL-CHEMICAL TREATMENT OF RAW MUNICIPAL WASTEWATER

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Contract No. 14-12-818
Project 11010 EYM
Program Element 1B2033

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Prepared for
OFFICE OF RESEARCH AND MONITORING
U.S. ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

For sale by the Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402 - Price $1.05

ABSTRACT

Physical-chemical treatment of raw wastewater in a 50,000 to 100,000 gpd pilot plant consisted of two-stage lime precipitation with intermediate recarbonation, filtration, pH control, ion exchange or breakpoint chlorination for nitrogen removal and carbon adsorption. The complete system with ion exchange removed 98% of the phosphorus, 95% of the organics (COD) and 78% of the total nitrogen. With breakpoint chlorination, the complete system removed approximately 98% of the phosphorus, 94% of the organics (COD) and 86% of the total nitrogen.

Lime treatment with approximately 300 mg/l of CaO increased the wastewater pH to about 11.5, removed approximately 96% of the phosphorus and 80% of the BOD, TOC and COD. Recarbonation with 120 mg/l of CO_2 and with 5 mg/l of Fe^{+++} as a flocculant reduced the pH to 10 and precipitated excess Ca^{++} as $CaCO_3$. The $CaCO_3$ was settled in a second settler. Dual media filtration (18" of 0.9 mm coal over 6" of 0.45 mm sand) decreased effluent suspended solids to less than 5 mg/l and total phosphorus to less than 0.15 mg/l of P. Addition of 10 mg/l of chlorine to the influent filter controlled biological growth within the filter and produced filter runs of greater than 50 hours.

With extensive operator surveillance, the clinoptilolite exchange mineral reduced the ammonia to less than 1 mg/l as NH_4^+-N. Breakpoint chlorination oxidized the ammonia to N_2 leaving a residual NH_3-N concentration of less than 0.4 mg/l. The total nitrogen residual for the physical-chemical treatment with breakpoint chlorination varied from 2 to 3 mg/l as N.

The 20 mg/l of soluble BOD entering the granular carbon columns produced anaerobic biological growth on the carbon. Carbon loadings as high as 0.3 pounds of dissolved TOC per pound of carbon was obtained during the study with an effluent TOC of approximately 8 mg/l. Heavy biological growth developed during the investigation which contributed to high carbon losses during back wash and heavy H_2S production. Breakpoint chlorination ahead of carbon adsorption minimized the biological activity. The organic loading with breakpoint chlorination was approximately 0.24 pounds of dissolved TOC per pound of carbon at an effluent TOC concentration of approximately 10 mg/l.

This report was submitted in partial fulfillment of Project 11010 EYM and Contract No. 14-12-818 by the Department of Environmental Services, Government of the District of Columbia under the sponsorship of the Environmental Protection Agency. Work was completed as of September 1971.

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ACKNOWLEDGMENTS

Walter W. Schuk of the Environmental Protection Agency developed the control system described in the study and is acknowledged with sincere thanks.

The operation of the pilot system with analytical support was performed by the EPA-DC Pilot Plant staff under the supervision of the Chief Operator, George D. Gray, Supervisory Engineering Technician, Robert A. Hallbrook and Chief Chemist, Howard P. Warner.

The authors wish to acknowledge Battelle-Northwest of Richland, Washington, for the use of their trailer-mounted selective ion exchange system and to especially thank B.W. Mercer, Senior Research Engineer, and R.C. Arnett, Research Engineer, of Battelle-Northwest for the initial operation and the training of the pilot plant staff on the exchange system.

SECTION I

CONCLUSIONS

1. Physical-chemical treatment consisting of two-stage lime precipitation with intermediate recarbonation, filtration, pH control, selective ion exchange or breakpoint chlorination and carbon adsorption removed approximately 92% of the TOC, 96% of the BOD, 95% of the COD, 97% of the suspended solids and 98% of the total phosphorus. With ion exchange, the system removed 78% of the total nitrogen from the District of Columbia raw wastewater. With breakpoint chlorination, the system removed 86% of the total nitrogen. The pollutant residuals for seventeen months of treatment averaged approximately 8 mg/l TOC, 6 mg/l of BOD, 16 mg/l of COD, 4 mg/l of suspended solids, 0.14 mg/l of total phosphorus as P. With ion exchange for nitrogen removal, the total residual averaged 4.6 mg/l of total nitrogen. With breakpoint chlorination for nitrogen removal, the total residual nitrogen averaged 2.8 mg/l.

2. In the study, lime precipitation removed approximately 80% of the TOC, BOD and COD, 88% of the suspended solids, 97% of the total phosphorus and approximately 30% of the total nitrogen.

3. Filtration of the lime clarified wastewater increased the overall removal of pollutants by 1-9%. As examples, the suspended solids removals increased from 88 to 97%, while the total phosphorus removal increased from 97 to 98%.

4. With minimal operator surveillance, the ion exchange process located ahead of carbon adsorption, removed 75% of the influent ammonia with an average residual of 3.0 mg/l of NH_4^+-N. However, with careful operator surveillance, the ion exchange process reduced the NH_4^+-N residuals to less than 1 mg/l (greater than 90% removal) and the total nitrogen removal to over 85%. The ion exchange process also removed from 15 to 35% of the residual "soluble" organics from the lime clarified and filtered wastewater and increased the cumulative organic removal to more than 85%.

5. The breakpoint chlorination of ammonia to nitrogen was carried out usually in a pH range of 6 to 8. The chlorination process with good pH control oxidized 10-15 mg/l of NH_4^+-N to N_2 gas. With good pH control (steady flow) effluent NH_4^+-N averaged less than 0.4 mg/l. For the entire study, the effluent NH_4^+-N averaged 0.46 mg/l. NO_3^--N produced as a by-product was approximately 0.6 mg/l. Essentially no NCl_3 was detected in the effluent at a reaction pH of approximately 7.0. The dose weight ratio of $Cl:NH_4^+$-N required for the breakpoint was approximately 9:1.

6. The experimental system with a 12 minute reactor time exhibited control problems especially during operation with diurnal flow, and

also with a high influent pH (9-10). Ammonia breakthrough occurred during periods of poor process control. An in-line mixer with small reaction detention time is recommended for improved process control and efficient mixing.

7. NaOH addition neutralized the acid produced during chlorination to maintain approximately a neutral reaction pH.

8. Chlorination did not appreciably oxidize the soluble organics in the wastewater.

9. With virgin carbon, adsorption removed between 75 and 80% of the organics entering the adsorption columns with average residuals of 3.7 mg/l of BOD and TOC, and 8.2 mg/l of COD during the first month. With organic loading and biological growth, residuals after adsorption increased to 8 mg/l of BOD and TOC, and 19 mg/l of COD for the month before the first replacement of spent carbon. The pattern of the low organic residuals after an activated carbon replacement gradually increasing with increasing organic loading on the activated carbon repeated itself through subsequent carbon replacement cycles.

10. For operation without chlorine addition to carbon column influent, heavy anaerobic biological growth occurred and H_2S appeared (2-3 mg/l) in the effluent. The biological slimes coated the carbon granules, produced high pressure losses (25 psig across the first column in 24 hours) and caused excessive carbon losses during backwash.

11. The application of breakpoint chlorination ahead of carbon adsorption minimized the biological activity, eliminated the high pressure losses across the first column (less than 10 psig in 48 hours) and produced hydraulic operation in the carbon system comparable to that obtained during earlier tertiary carbon treatment.

12. The organic loading on the activated carbon without chlorine in the influent water was 0.3 lb of dissolved TOC per lb of carbon at an effluent TOC of approximately 8 mg/l. The organic loading on the carbon during breakpoint chlorination (chlorine in the influent to adsorption) was 0.24 lb of dissolved TOC per lb of carbon at effluent TOC of approximately 10 mg/l.

13. The backwashing sequence with high pH (11.5) water applied to the adsorption system did not eliminate biological activity in the carbon. Thus, determination of the effect of the biological activity on the product quality requires additional work.

14. The solids production for the two-stage lime clarification was a function of lime dose and wastewater content. Typical sludge production for a lime dosage of 350 mg/l was approximately 7.5 lb of solids per million gallons of treated water.

SECTION II

RECOMMENDATIONS

1. In future work, the optimum design requirements for lime clarification needs to be determined including maximum sedimentation rates and the effect of reactor solids concentration, pH and temperature on the rate of precipitation and flocculation of calcium carbonate, calcium hydroxyl apetite and magnesium hydroxide from the wastewater.

2. In the second stage lime clarification, the effects of flue gas (8% CO_2) on the recarbonation flocculation and second stage sedimentation requires further evaluation for proper system design.

3. In the ion exchange process, the brine system which may include reuse or disposal of the brine solution requires further study. Air stripping of the ammonia from the brine with subsequent absorption from the air in phosphoric acid and precipitation as ammonium phosphate for final disposal should be evaluated.

4. The long term attrition losses of the clinoptilolite exchange mineral and the long term effects of repeated regeneration on the exchange capacity of the mineral also needs to be determined.

5. The kinetics of breakpoint chlorination needs further study for optimum breakpoint reactor design and control.

6. The effect of biological growth in carbon adsorption especially on carbon losses and H_2S production needs further study. Alternate methods other than chlorination for control of the H_2S production and slime gorwth should be considered and evaluated. Possible alternates include upflow carbon columns with oxygen addition or nitrate addition in pressured downflow columns.

7. Solids handling characteristics such as thickening, dewatering and lime recovery needs to be studied. Centrifugation for classifications (separation) of carbonate solids from non-carbonate solids and the handling of non-carbonate solids in the centrate should be included in the evaluation.

8. An automated control system for physical-chemical treatment especially for the breakpoint chlorination process needs to be developed.

9. Since the ion exchange and the carbon columns also act as filters, operation without the dual-media filters should be conducted to determine whether losses in treatment efficiency occur. The filters should be relocated to remove suspended solids in the effluent from carbon adsorption and thus increase treatment efficiency.

SECTION III

INTRODUCTION

In the early work on advanced treatment of secondary effluents, the product water from granular carbon treatment contained organic materials apparently refractory to carbon adsorption (1). Addition of chemical clarification to the tertiary treatment system (2) for phosphorus removal eliminated from secondary effluents most of the organics refractory to adsorption and produced water, after carbon adsorption, with residual total organic carbon (TOC) concentrations of less than 1 mg/l. Clarification with lime or alum insolubilized the phosphorus and flocculated the colloidal organic and phosphorus materials that were too small to efficiently filter, and too large to diffuse into the pores of the carbon granule. In that early study, primary effluent, fed to a tertiary treatment system, revealed that clarification and filtration to remove the colloidal material from the primary effluent also produced moderately low residual organic concentrations after carbon adsorption.

Recently, several laboratory and pilot scale studies (3, 4, 5, 6, 7, 8, and 9) were completed on physical-chemical treatment of raw or primary wastewater. The physical-chemical treatment in these studies usually consisted of chemical clarification and dual or multi-media filtration for solids and phosphorus removal, followed by granular or powered carbon adsorption to remove the dissolved organics. Physical-chemical treatment also removed particulate nitrogen by clarification, soluble organic nitrogen by carbon adsorption, and nitrate, if present, by biological denitrification on the carbon (9).

In these studies, the clarification process on either primary effluent or raw wastewater employed lime precipitation or metallic salts, such as $FeCl_3$ or alum. In lime precipitation, two treatment options are available: the two-stage high pH lime process (10), usually above pH 11.5, with intermediate recarbonation to remove excess calcium ions from the primary (first) stage, and the single-stage precipitation (8) at pH as low as 9.5. The high pH lime process was usually applied in waters of moderate alkalinity (100-200 mg/l as $CaCO_3$) and produced efficient solids removal and very low phosphorus residuals of less than 0.2 mg/l as P. In hard waters with alkalinities above 250 mg/l, the low pH single-stage lime process produces efficient solids removal and phosphorus residuals of approximately 0.5 mg/l.

In waters with moderate alkalinities, the low pH lime process requires supplemental flocculants, such as polymers or $FeCl_3$, to produce efficient clarification and phosphorus residuals of approximately 1 mg/l. Ferric chloride, with or without polymer, efficiently clarified raw or primary wastewater (9) and produced phosphorus residuals of 0.6 to 1 mg/l.

After the removal of the colloidal substances by clarification and filtration, carbon initially physically adsorbed most of the dissolved organics. In continuous treatment, the build-up of soluble organic material on the carbon rapidly promoted substantial biological activity within the adsorption system and degraded the product quality. The growth also occurred on powdered carbon that was recirculated (11). The biological activity on the granular carbon particle, as has been reported (12), increased the carbon loading before regeneration.

However, the metabolic end products and sluffing of excess cell mass from the carbon degraded the water quality by increasing both the residual solids and organic concentrations (2). The biological growth also increased the pressure drop across the carbon column. Expanded upflow beds of carbon have been employed to minimize pressure losses and backwash requirements (9), but the microbial end products were still released into the product water and the slimes coated the carbon granules.

In domestic raw wastewaters, most of the soluble nitrogen exists as ammonia or its predecessor urea, and is not removed by clarification or adsorption. Thus complete physical-chemical treatment requires an ammonia removal process. Three physical-chemical processes are available for ammonia removal: air stripping of the water above pH 10.5 (13), breakpoint chlorination (14), and selective ion exchange (15).

In the selection of an ammonia removal process for complete physical-chemical treatment, air stripping (13) of the ammonia was not effective in cold weather. The ammonia volatility in an air-water system decreased with decreasing temperature and the stripping efficiency decreased sharply for any selected air to liquid loading rate. Calcium carbonate scaling also gradually decreased the removal efficiency and increased the maintenance costs. Thus ammonia stripping is not considered universally applicable because of temperature restrictions. Breakpoint chlorination (14) and selective ion exchange (15), however, provided potential all-weather processes for ammonia removal.

The selective ion-exchange process, with a natural zeolite, clinoptilolite, was developed by Battelle-Northwest for ammonia removal (15). The clinoptilolite exchanged Na^+ or Ca^+ ions for NH_4^+ ions in the wastewater.

The Battelle ion-exchange process was carried out in columns packed with the 20 x 50 mesh clinoptilolite. The Clinoptilolite, mined as a rock from the Baroid Division of National Lead's deposits at Hector, California was crushed and sieved to a 20 x 50 mesh particle size. The columns were regenerated by a lime-salt mixture. Concentrated ammonia was removed from the reused regenerant by air stripping. The process reduced the ammonia concentrations in wastewater to less than 1 mg/l. Although selective for ammonia, the zeolite also removed cations present in the water. Studies by Battelle-Northwest (16)

reveal that with an influent Ca^{++} of 30 mg/l and NH_4^+-N of 14 mg/l half the ion exchange capacity is used by Ca^{++} ions.

A recent laboratory study (14) showed that breakpoint chlorination with proper pH control and mixing provided a physical-chemical method for removing NH_4^+ from wastewaters by oxidizing the NH_4^+ to N_2 gas. The $Cl:NH_3$-N dosage weight ratio was in the range 8:1 to 10:1 as compared with the stoichiometric ratio 7.6:1. The excess Cl_2 for breakpoint, above that needed for stoichiometric oxidation, varied inversely with the degree of pre-treatment of the wastewater. The study also showed that the undesirable side reactions which produces NO_3^- was favored by high reaction pH and that the production of NCl_3 was favored by a combination of low pH and excess Cl_2. Hence, to keep the nuisance residuals to a minimum, the reaction pH was maintained near pH 7.0.

In a later pilot study (17) on secondary effluent, rapid mixing was necessary to efficiently disperse the Cl_2 in the process water. With poor mixing, localized high Cl_2 concentrations caused excessive NCl_3 formation even when NaOH or $Ca(OH)_2$ was used to maintain the pH at 7. Thus for successful operation of the breakpoint process with a minimum of NO_3^- and NCl_3 production, the reaction must be well mixed, its pH controlled in the pH range 6-8 and the excess Cl_2 kept to a minimum.

While physical-chemical treatment has been applied to both raw wastewater and primary effluents, it is most likely to be applied directly to raw wastewater as the more economical system. Thus, a study of complete physical-chemical treatment was conducted on domestic raw wastewater at the EPA-DC Pilot Plant in Washington, D.C. to remove carbon, phosphorus, and nitrogen. Since very low phosphorus residuals were needed, the two-stage high pH lime process was employed for clarification. Downflow granular carbon columns were used for removal of the dissolved organics; selective ion exchange and breakpoint chlorination were separately evaluated for ammonia removal.

SECTION IV

EXPERIMENTAL

Pilot Systems

The initial automated pilot system (Figure 1) consisted of cyclone degritting, two-stage (high pH) lime precipitation with intermediate recarbonation, dual-media filtration, pH control, selective ion exchange, and downflow granular carbon adsorption. The precipitation process was designed for a nominal capacity of 100,000 gallons per day; the filtration, ion exchange, and carbon adsorption processes for 50,000 gallons per day. Later breakpoint chlorination was substituted for the ion-exchange process. When the system employed ion exchange for ammonia removal, a flow controller impressed a diurnal variation of approximately 3.2:1 maximum to minimum flow across the clarification process. Flow splitter boxes and level controllers reduced the flow from the precipitation process to the hydraulic capacity of the subsequent treatment processes while still maintaining the diurnal variation. Because of process control difficulties, the breakpoint chlorination process and therefore, the carbon columns were generally operated at a constant flow of 25 gpm when breakpoint was employed for nitrogen removal.

In the first-stage of the precipitation process, raw wastewater, lime slurry and recycled solids were turbine-mixed at 13 rpm (average reaction time of 40 minutes) in the internal reactor of an upflow flocculator-clarifier. The lime increased the wastewater pH to about 11.5 and precipitated bicarbonate, phosphate, and magnesium ions from the water as shown in equations 1-3.

$$Ca^{++} + HCO_3^- + OH^- \longrightarrow CaCO_3 + H_2O \qquad (1)$$

$$5Ca^{++} + 3H_2PO_4^- + 7OH \longrightarrow Ca_5OH(PO_4)_3 + 6H_2O \qquad (2)$$

$$Mg^{++} + 2OH^- \longrightarrow Mg(OH)_2 \qquad (3)$$

Sludge from the slurry pool at the bottom of the clarifier was recycled at a rate equal to 10% of the average influent flow. Waste rates of approximately 1.8% of the influent flow with solids concentrations of 30,000 to 50,000 mg/l maintained the solids balance of the slurry pool.

The limed water, after sedimentation, flowed through an open channel to recarbonation. Carbon dioxide below a turbine operating at 171 rpm, reduced the wastewater pH to approximately 10, and with an average contact period of 15 minutes, precipitated the excess calcium ions added in the liming (first) stage according to equation 4.

$$Ca^{++} + CO_2 + 2OH^- \longrightarrow CaCO_3 + H_2O \qquad (4)$$

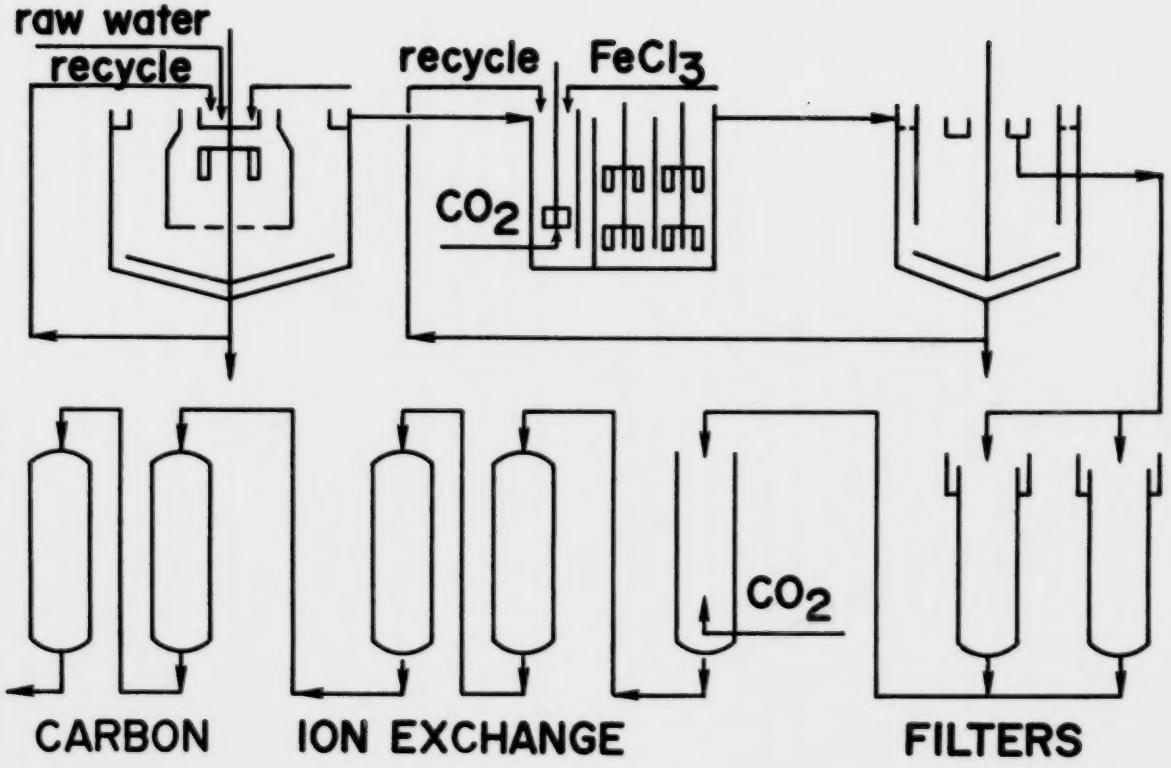

FIGURE 1 - Physical-Chemical Treatment Pilot Plant

Five mg/l of ferric ions, added in the first of the two external 24-minute flocculation basins, each turbine-mixed at 22 rpm, formed $Fe(OH)_3$ according to equation 5 and flocculated the precipitated calcium carbonate.

$$Fe^{+++} + 3HOH \longrightarrow Fe(OH)_3 + 3H^{+} \qquad (5)$$

After flocculation, the water flowed to a perpherial feed circular clarifier. Settled slurry recycled from the bottom of the settler to recarbonation at a flow rate equal to 10% of the average influent flow provided nuclei for the calcium carbonate precipitation in the recarbonation tank. Wasting at flows approximately equal to 1.9% of the influent flow maintained the solids balance of the slurry pool in the settler.

The overflow from the second-stage clarifier, was pumped to a distribution box ahead of the two filters. It then flowed by gravity through two dual-media filters packed with 18 inches of 0.9 mm coal over 6 inches of 0.45 mm sand. When pressure losses across the filter exceeded 9 feet of head, a surface wash at 3 gpm/ft^2 and a sequenced backwash at up to 20 gpm/ft^2 automatically cleaned the filter for ten minutes and returned it to service.

In operation with selective ion exchange, carbon dioxide added after filtration, reduced the pH of the filtered water to 7-8 in the pH control tank. The water then was pumped to the ion exchange followed by carbon adsorption or to the carbon adsorption processes followed by ion exchange treatment. The trailer-mounted ion-exchange system was not fully automated and required continuous operator surveillance for efficient ammonia removals. Thus, the exchange system was operated intermittently and not always at peak efficiency.

In the ion-exchange process, the Battelle pilot plant, consisted of three exchange columns, a stripping tower, regenerant mixing tank, air blower, and air heater. Figure 2 is a flow diagram showing the ion-exchange system. The exchange columns were 39 inches in diameter and eight ft. tall. Each column was packed with approximately 1870 pounds of zeolite and was operated under a pressure of 35 p.s.i.g.

The NH_3 stripping tower was a 43-inch diameter fiberglass tower packed with seven ft. of 1-inch polypropylene Intalox saddles. The tower drained into a 200 gal. agitated tank, where lime was added under pH control. Air for the stripping tower was supplied by the 10-h.p. blower and was heated by a 60-k.w. heater.

A compact piping cross header, installed underneath the trailer, contained 36 electrically-operated ball valves, which permitted the liquid flow to be routed anywhere in the process.

The influent stream, controlled at pH 7.0-7.5, was pumped downflow through two clinoptilolite beds in series at loading rates from 2.4 to

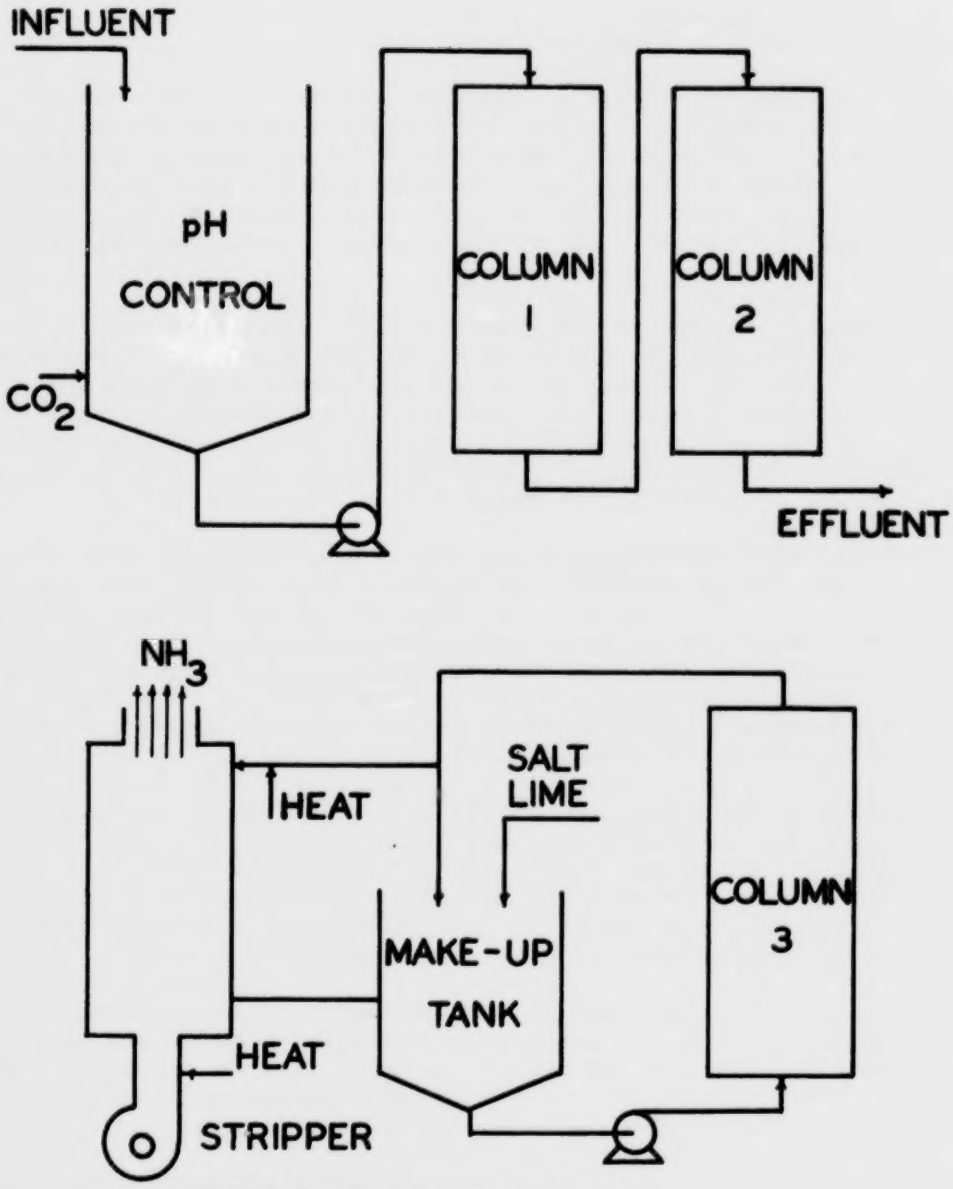

FIGURE 2 - Ion Exchange Process

6.3 gpm/ft^2. The operation for the three ion-exchange columns was:

1. Two beds were in service downflow while the third was being regenerated.
2. After the first bed in service approached maximum ammonia loading (ammonia in effluent was 90% of influent concentration), it was taken out of service and the second bed was placed in the number two position.
3. A column was regenerated by pumping a solution of Na^+ and Ca^{++} ions (sodium chloride and lime) at a pH of 11.0 upflow through the zeolite.

The regenerant was recirculated through the bed at a loading rate of 7.2 gpm/ft^2 for three hours to strip the NH_4^+ ions from the clinoptilolite as NH_3OH and to build up the ammonia concentration in the regenerant to approximately 500 mg/l NH_3-N. The regenerant flow was decreased to 3 gpm/ft^2 and then recycled through both the zeolite bed and the stripper until the NH_3-N was reduced to 20 mg/l (average time 12 hours). During regeneration, the pH was automatically maintained at 11.

A portion of the regenerant solution which remained in the mixing tank was reused from batch to batch. Following regeneration, the column was backwashed with ammonia free water to remove the lime deposits. The air stripper was operated at a liquid rate of 25 gpm with an air to liquid ratio of approximately 100 ft^3 of air per gal. of water.

The first five months of operation (82 days) were on lime clarified and filtered raw wastewater. In July 1970, the ion-exchange unit was placed after carbon adsorption in the physical-chemical system because the anaerobic growths on the carbon were converting organic nitrogen to ammonia. Thus, more ammonia was available for ion exchange on the zeolite after carbon adsorption. The air stripper was run with heated air (80^{o}F) for the first month and with ambient air during the remainder of its operation. Regenerant solution was not reused during one month (December) of cold weather operation.

After completing the studies on the ion-exchange system, breakpoint chlorination was evaluated as an alternate ammonia removal process. The breakpoint chlorination pilot system in this study (Figure 3) consisted of a 1200 gallon reactor, 4 feet in diameter, 12 feet tall with appropriate pumps, chlorine contactors and automatic controllers. The reactor vessel, a existing modified pH control tank, was larger than needed for chlorination. Only the bottom 3 feet (310 gallons) was used for the chlorination reactor. Mixing was provided by 3 propeller mixers mounted on a common shaft, driven by a 3 hp motor at 225 rpm. The pump on the effluent stream recycled 11 gallons back to the reactor. Chlorine was added to the recirculating water through a Wallace and Tiernan chlorinator and injector nozzle. The chlorine was added to process waters with pH control by NaOH addition and with proper mixing until a point was reached where the total dissolved residual chlorine

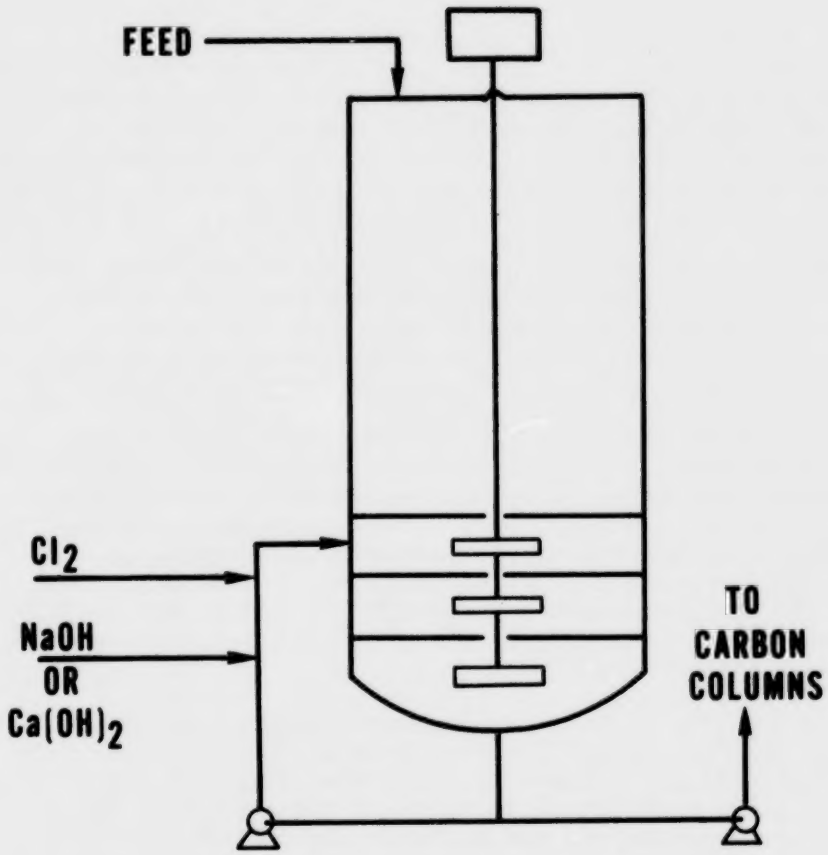

FIGURE 3 - Breakpoint Chlorination Reactor

reached a minimum and the NH_4^+ was oxidized chiefly to N_2 gas. The reaction to nitrogen gas proceded through monchloramine as described by the following equations.

$$Cl_2 + H_2O \longrightarrow HOCl + HCl \quad (6)$$

$$NH_4^+ + HOCl \longrightarrow NH_2Cl + H_2O + H^+ \quad (7)$$

$$2NH_2Cl + HOCl \longrightarrow N_2 + 3HCl + H_2O \quad (8)$$

The overall reaction was:

$$2NH_4^+ + 3HOCl \longrightarrow N_2 + 3HCl + 3H_2O + 2H^+ \quad (9)$$

Control of pH was needed because the type of chloramine formed and the ultimate oxidation product depends upon pH. Spectroscopic analysis (18, 19, 20, 21, 22) indicated that, in the pH range 7-8.5, monochloramine was the chief intermediate product. As the Cl_2 dose exceeded that for NH_2Cl formation, the NH_2Cl was oxidized directly to N_2 gas. If the pH is allowed to decrease below 7, increasing amounts of dichloramine were formed (equation 10). In the pH range of 4.5 and below, trichloramine was the chief product (equation 11). Nitrate was also produced in small quantities according to equation 12.

$$NH_2Cl + HOCl \longrightarrow NHCl_2 + H_2O \quad (10)$$

$$NHCl_2 + HOCl \longrightarrow NCl_3 + H_2O \quad (11)$$

$$4HOCl + NH_3 \longrightarrow HNO_3 + 4HCl + H_2O \quad (12)$$

The pH of the water in the reactor was automatically maintained by controlled pumping of a 1 to 2% NaOH solution into the line ahead of the chlorine injector. The NaOH feed rate was controlled by an inline pH probe on the discharged effluent.

A Technicon Autoanalyser was used to continuously monitor the NH_4^+-N concentration in the influent and effluent. The NH_4^+-N concentration in the influent was used to manually set the Cl_2 at a 9:1 Cl:N ratio and the NH_4^+-N concentration in the effluent was used to determine whether breakpoint was achieved. Periodic laboratory measurements of free and combined Cl_2 were performed on the process effluent to check pilot plant operation.

In the five months of the study, the feed to the system was lime-clarified filtered raw wastewater. For the first four months of operation, the flow rate was a constant 25 gpm. The first month of operation revealed that breakpoint control was difficult because of the large reactor detention time of 12 minutes. Adjusting the pH to 7.0 with CO_2 before entering the breakpoint reactor improved process control.

Hence, after one month of continuous operation with an influent pH of 9 to 10, CO_2 was used in a Kenics in-line static mixer to automatically preadjust the influent wastewaters pH from 9-10 to 7. The process was operated continuously for 3 months with CO_2 preadjustment.

Since CO_2 increased base usage, the process was further modified for the last month of operation. A second chlorinator was installed and Cl_2 was added in place of CO_2 for preadjusting pH. A diurnal flow variation with a maximum of 55 gpm and a minimum of 22 gpm was also impressed across the system.

The flow from either the ion-exchange process or from the pH control or breakpoint tank was pumped at 50 psig through four downflow carbon columns each packed with 840 pounds of 8 x 30 mesh granular carbon. The carbon was supported by a 50 mesh stainless-steel screen on a gravel bed. The first column was backwashed and surface-washed on a daily basis with a quantity of water equal to about four percent of the product water. After four months of operation, the use of a high pH (11.5) backwash was tested on alternate days with the product water to minimize biological activity on the carbon. The other columns were also washed once a week with the high pH water. To stimulate two-stage carbon treatment, the spent carbon was replaced with virgin carbon in two columns at a time. In the replacement cycle, the replaced carbon (2 columns) was located at the end of the carbon system as the second carbon stage and the partially loaded carbon (2 columns) in the original second stage was relocated as the first carbon stage. A flexible piping manifold permitted the counter-current operation and also allowed the isolation and the backwash of individual carbon columns without interruption of the process flow. The carbon after replacement was not regenerated.

Analytical Procedures

In the first four months of the study with ion exchange in the system all samples for analysis were manually composited over 24 hours. To reduce the analytical load, samples for Ca^{++}, Mg^{++}, total phosphorus, NH_3, COD, and TOC were then composited over 48 hours for the remainder of the ion-exchange operation. Samples for COD, TKN, suspended solids, and $NO_3^- + NO_2^-$ were always composited over 24 hours. During compositing, all samples were stored at 3^oC to minimize biological activity. In the operation with breakpoint chlorination, all samples were composited over 24 hours.

In the laboratory, the total phosphorus were determined by the persulfate method (23); BOD_5 by the probe method (24). The Ca^{++} and Mg^{++} analyses was measured on a Perkin and Elmer Model 303 Atomic Adsorption unit (24). Ammonia (24) and nitrate-nitrite (25) were determined on a Technicon Automatic Analyzer, and the TOC was measured on a Beckman Carbonaceous Analyzer (26). All other analyses including the Phenophthalein (P) and methyl orange (M.O.) alkalinities employed Standard Methods (27).

The chlorination study required field measurement for NH_4^+-N, which was analyzed on a programmed Technicon Automatic Analyzer (24). Free and combined chlorine were measured by the Modified Palin Method (28) with N, N-diethyl-p-phenylenediamine oxalate as the indicator.

SECTION V

PROCESS OPERATIONS

The intake for the pilot plant was located at the head of the main plant's grit chamber. Solids in the wastewater continually fouled the intake pumps of the pilot plant. After the first month of operation, bar screens were placed over the intake. Rags and other refuse clogged the screens and filtered solids from the water. The pilot plant's efficient cyclone degritter also removed solids from the influent. Thus, the feed to the physical-chemical pilot plant contained less solids and particulate organics than the normal raw plant influent.

The normal operating flows, hydraulic loadings and detention times for the physical-chemical system are shown in Table 1. While the pilot plant included only physical-chemical processes, biological activity occurred within the plant and, as described in this section, altered the operation of some of the processes.

Clarification and Filtration Operation

Two-stage lime precipitation of the D.C. raw wastewater was a very stable process as long as the wastewater pH was above 11.3. If the lime slurry feed to the first stage reactor was interrupted or the lime concentration reduced, the resumption of the appropriate lime dose regained the product water quality within a few hours without biological activity. The average or median monthly operating variables, chemical requirements, and sludge wasting rates are summarized in Table 2. The lime CaO dosage and CO_2 dosage for recarbonation during the entire operation (Table 2) was approximately 300 mg/l and 120 mg/l, respectively.

The lime dosage from the slurry tank of a gravimetric lime feeder was controlled by flow-proportional pH control, flow-proportional alkalinity control, or flow-proportional conductivity control. The signal controlling the CaO dosage was produced by multiplying a feed-forward signal proportional to plant flow by a feed back signal from a pH, alkalinity or conductivity controller. The flow-proportional pH control provided the best lime feeding system. The same approach was applied to the CO_2 feed.

The maximum (rain peak) overflow rates in the first stage of clarification was 1450 gal/day/ft^2; in the second stage, 1770 gal/day/ft^2. The solids wasting usually ranged from 1.7 to 1.9% of the influent plant flow for the first stage and 1.9-2.1% for the second stage. The second stage (recarbonation) wasting was pumped to the first stage and wasted at high pH with the first stage solids. The concentration of solids in the combined sludge (first stage) varied from 30,000 to 50,000 mg/l. The 10% recycle of sludge from the clarification zones to the precipitation reactors produced reactor solids varying from

TABLE 1

PILOT PLANT HYDRAULIC LOADINGS

	Flow gal./min.	Hydraulic loading rate	Detention Time
Lime Precipitation			
Stage 1			
Dry weather flow	45 min.	475 gpd/ft^2	
	70 ave.	725 gpd/ft^2	
	105 max.	1100 gpd/ft^2	4.4 hrs.
Rain peak	140	1450 gpd/ft^2	
Primary mixing	70 ave.		40 min.
Stage 2			
Dry weather flow	45 min.	575 gpd/ft^2	
	70 ave.	885 gpd/ft^2	
	105 max.	1340 gpd/ft^2	2.8 hrs.
Rain peak	140	1770 gpd/ft^2	
Recarbonation	70 ave.		15 min.
Flocculation (2 basins)	70 ave.		24 min. ea.
Filtration			
	20 min.	1.7 gpm/ft^2	
2 Filters	35 ave.	3.0 gpm/ft^2	26.3 min.
	52 max.	4.5 gpm/ft^2	
Neutralization	35 ave.		30 min.
Ion Exchange	20 min.	2.4 gpm/ft^2	
	35 ave.	4.2 gpm/ft^2	16 min.
	52 max.	6.3 gpm/ft^2	
Breakpoint Chlorination[1]	25 ave.		12 min.
Carbon Adsorption	20 min.	4.0 gpm/ft^2	
	35 ave.	7.0 gpm/ft^2	27 min.
	52 max.	10.4 gpm/ft^2	

1 Chlorination and subsequent adsorption usually operated at a constant rate of 25 gpm during system operation with breakpoint chlorination.

TABLE 2

OPERATING VARIABLES FOR TWO-STAGE LIME CLARIFICATION

Month	Alkalinity	Lime Dose	First Stage	Recarbonation with CO_2	Second Stage	Neutralization with CO_2	First Stage Waste	Second Stage Waste
	mg/l $CaCO_3$	mg/l CaO	pH	mg/l CO_2	pH	pH	% of Inf.	% of Inf.
Mar. 70			11.8		10.4	7.1		
Apr. 70			11.7		10.7	7.2		
May 70	126			236.0		7.0	2.8	2.1
June 70	131	289	11.7	192.0	10.1	7.3	1.8	2.0
July 70	129	360	11.7	121.0	10.1	7.3	1.7	2.0
Aug. 70	147	320	11.4	74.3	10.1	7.5	1.7	2.0
Sept. 70	153	280	11.4	107.0	10.1	7.5	1.8	2.0
Oct. 70	161	370	11.5	95.6	10.1	7.7	1.9	2.0
Nov. 70	142	300	11.4	63.0	10.2	7.3	1.8	1.9
Dec. 70	147	240	11.3	72.5	10.1	7.4	1.8	1.9
Feb. 71	135	259	11.4	126	9.7	---	1.8	1.9
Mar. 71	127	251	11.4	93	10.0	---	1.8	1.9
Apr. 71	134	266	11.3	173	10.0	---	1.8	1.9
May 71	127	310	11.4	138	10.0	7.0	1.8	1.9
June 71	129	306	11.3	124	10.0	7.0	1.8	1.8
July 71	140	375	11.3	110	10.1	7.0	1.8	1.8
Aug. 71		338	11.4	104	9.8	---	1.8	1.8

3000 to 5000 mg/l for operation with the above sludge wasting rates. The 5 mg/l of Fe^{+++} produced effective flocculation in the second stage with suspended solids carryover in the second stage overflow of about 20 mg/l.

As the water temperature increased in the spring and summer, microbial growths occurred throughout the second stage clarifier at pH 10 but not in the first stage at pH 11.5. The growths, however, did not reduce clarification removal efficiencies.

The daily performance of the clarification system (Figure 4, 5, 6) indicated the stability of the two stage lime clarification process. The process typically removed 80% of the organics, 96% of the phosphorus and 88% of the suspended solids. The wide variations in the influent concentrations of phosphorus, organics (COD) and suspended solids did not significantly alter process performance or reliability.

The sludge production (Figure 7) in the process varied as a function of wastewater alkalinity, influent phosphorus and magnesium concentrations, influent suspended solids and lime dose. For a wasting rate of 1.8% from the first stage and with the maximum solids concentration in the waste slurry, the sludge production was approximately 7.5 pounds of total solids per thousand gallons of treated water (900 mg/l).

With efficient lime clarification and nominal filter loadings of 3.0 gpm/ft^2, filter runs of more than 50 hours occurred in the early spring. With increasing water temperatures, the growth of biological slimes at pH 10 within the filters and in the effluent from lime clarification gradually decreased the length of the filter runs to less than 12 hours. Ten mg/l of chlorine, added to the influent of the filters to control the slimes restored the filter runs to about 50 hours.

Ion-Exchange Operation

The ion-exchange system exhibited mechanical problems and required continual surveillance for optimum operation. Because of mechanical problems, the unit was operated for 120 days during the ten month test period. The average run lasted 24 hours before switching columns. With four hours of operator surveillance, ammonia removals (daily composites) for the intermittent operation (Figure 8) averaged 75% with residuals of 3.0 mg/l NH_4^+-N. Small amounts of COD and phosphorus were removed from the wastewater by the zeolite bed (Table 3). The suspended solids, however, increased and an increased turbidity appeared in the effluent. The turbidity was produced by lime deposits from poor regenerations.

The large fluctuations in the daily effluent NH_4^+ concentrations revealed the effects of minimum manpower for the ion-exchange operation. Electrical valve malfunctions were frequently responsible for mixing

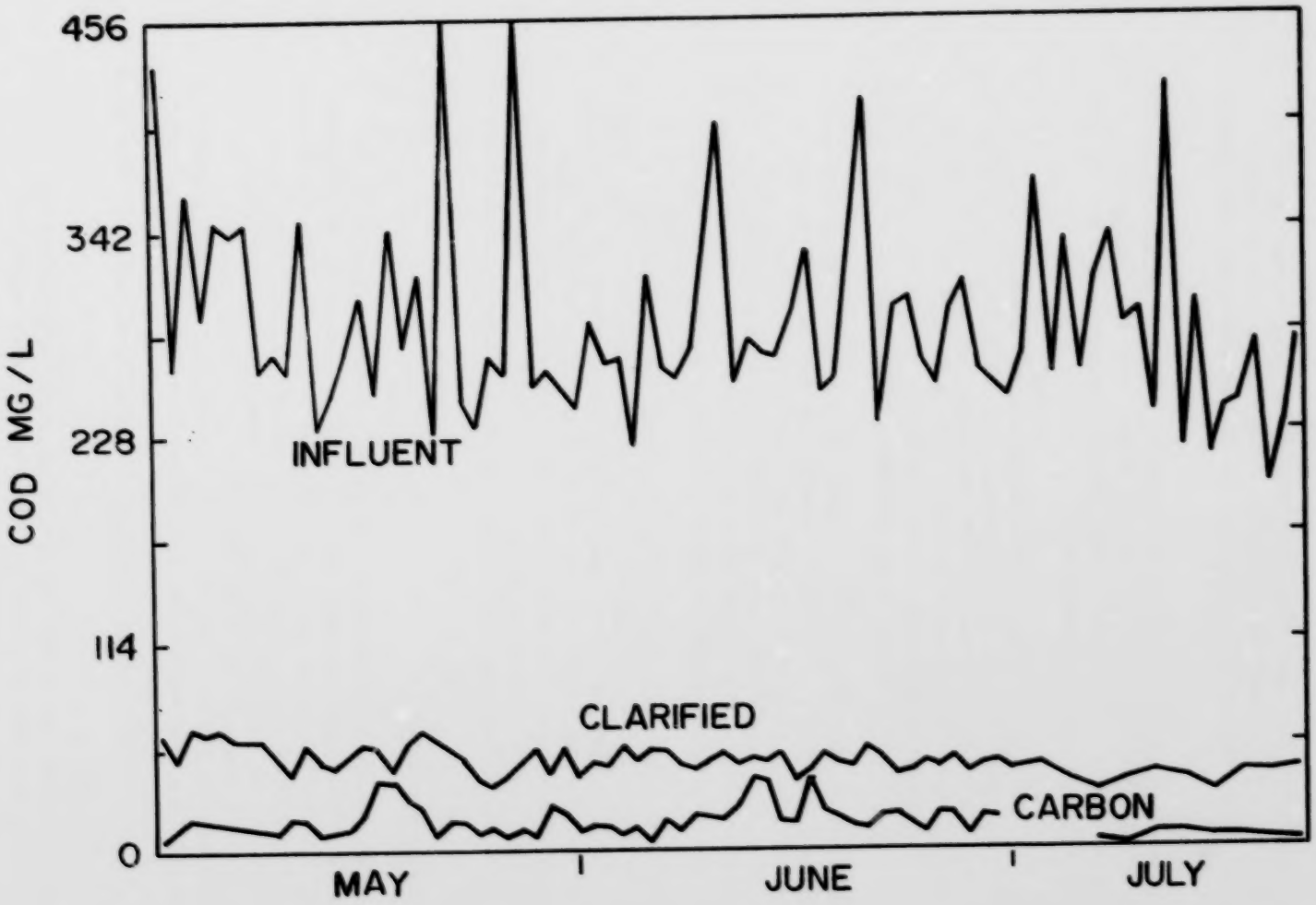

FIGURE 4 - Daily Removals of COD in Physical-Chemical Treatment

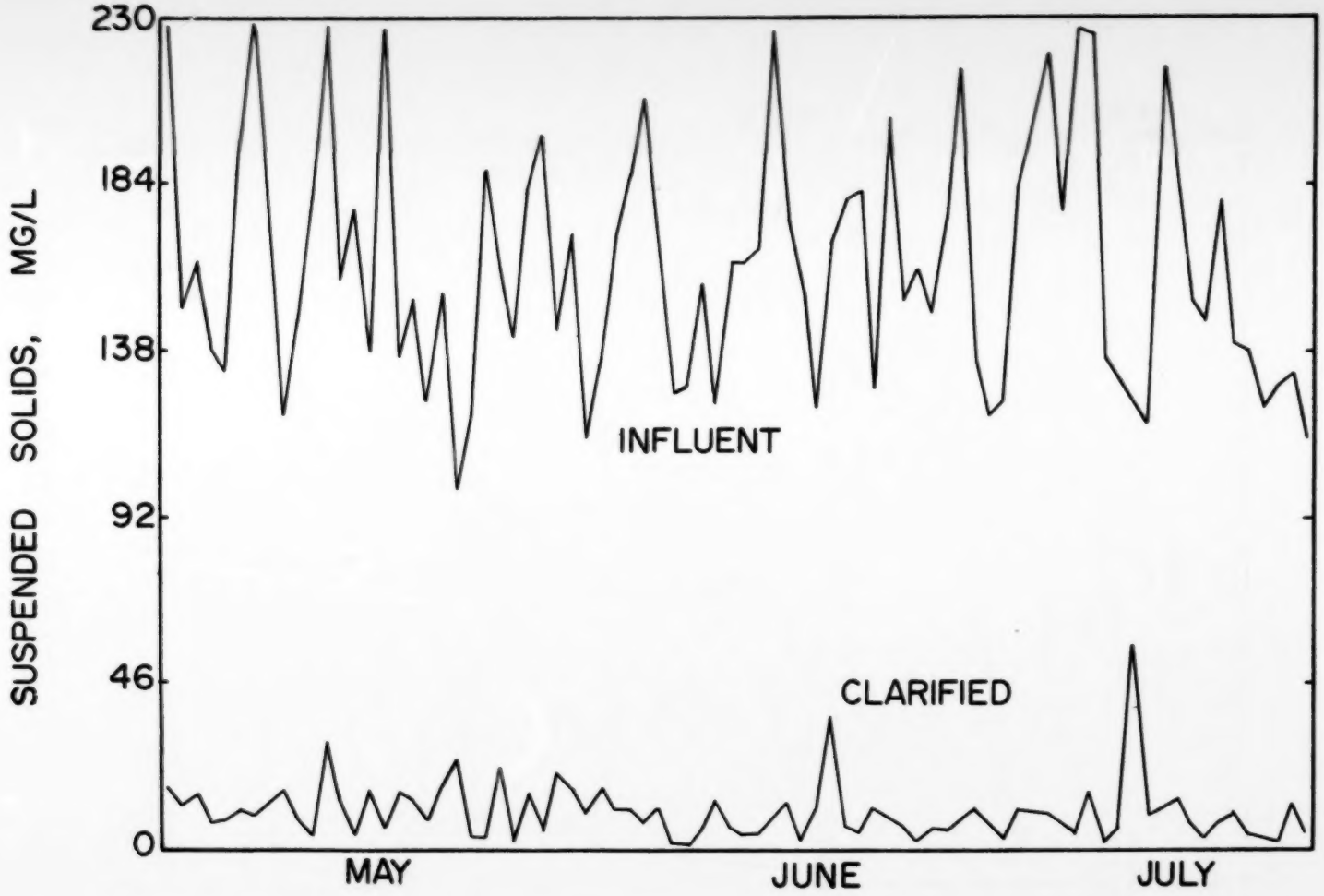

FIGURE 5 - Daily Removal of Suspended Solids in Lime Clarification

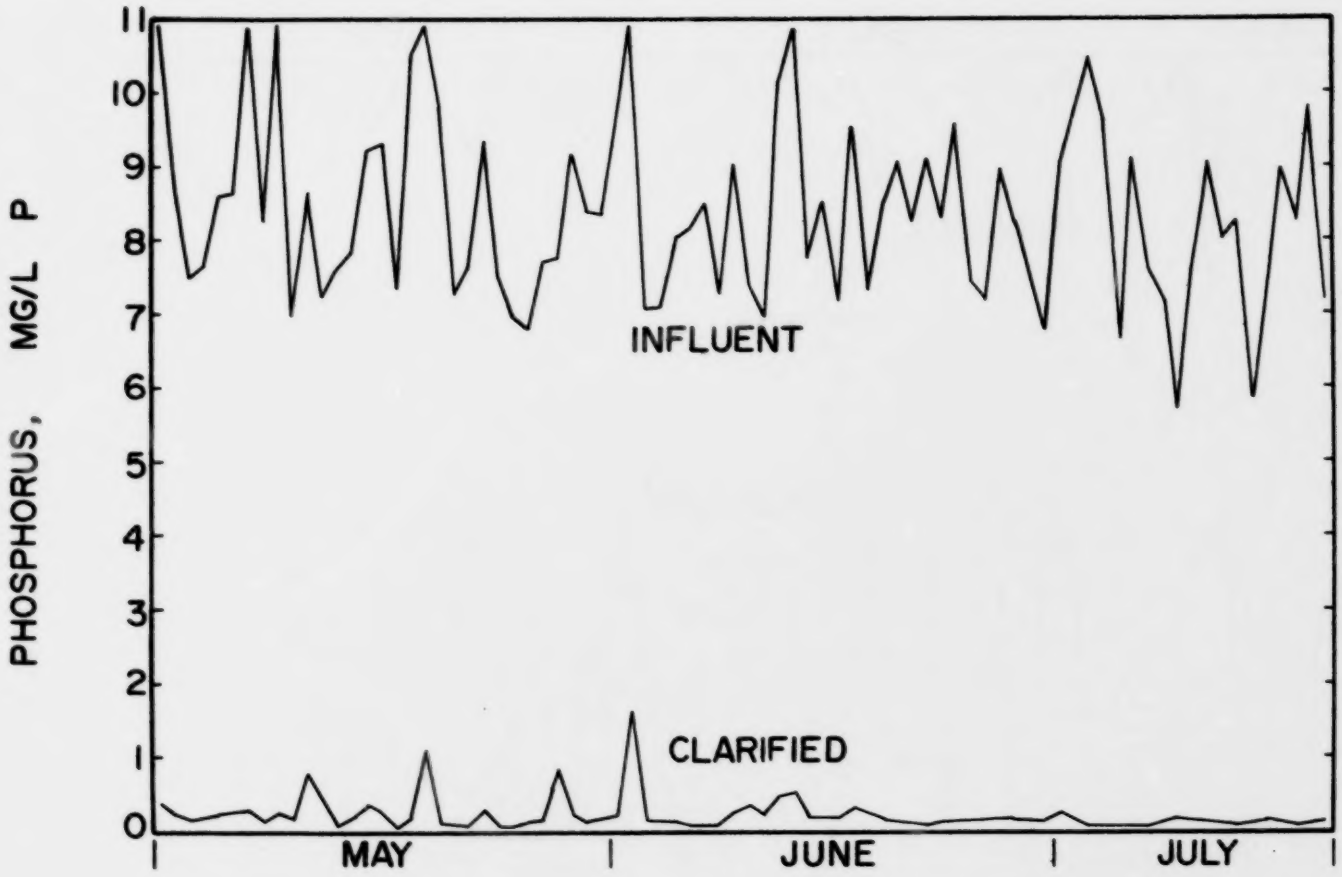

FIGURE 6 - Daily Removal of Phosphorus in Lime Clarification

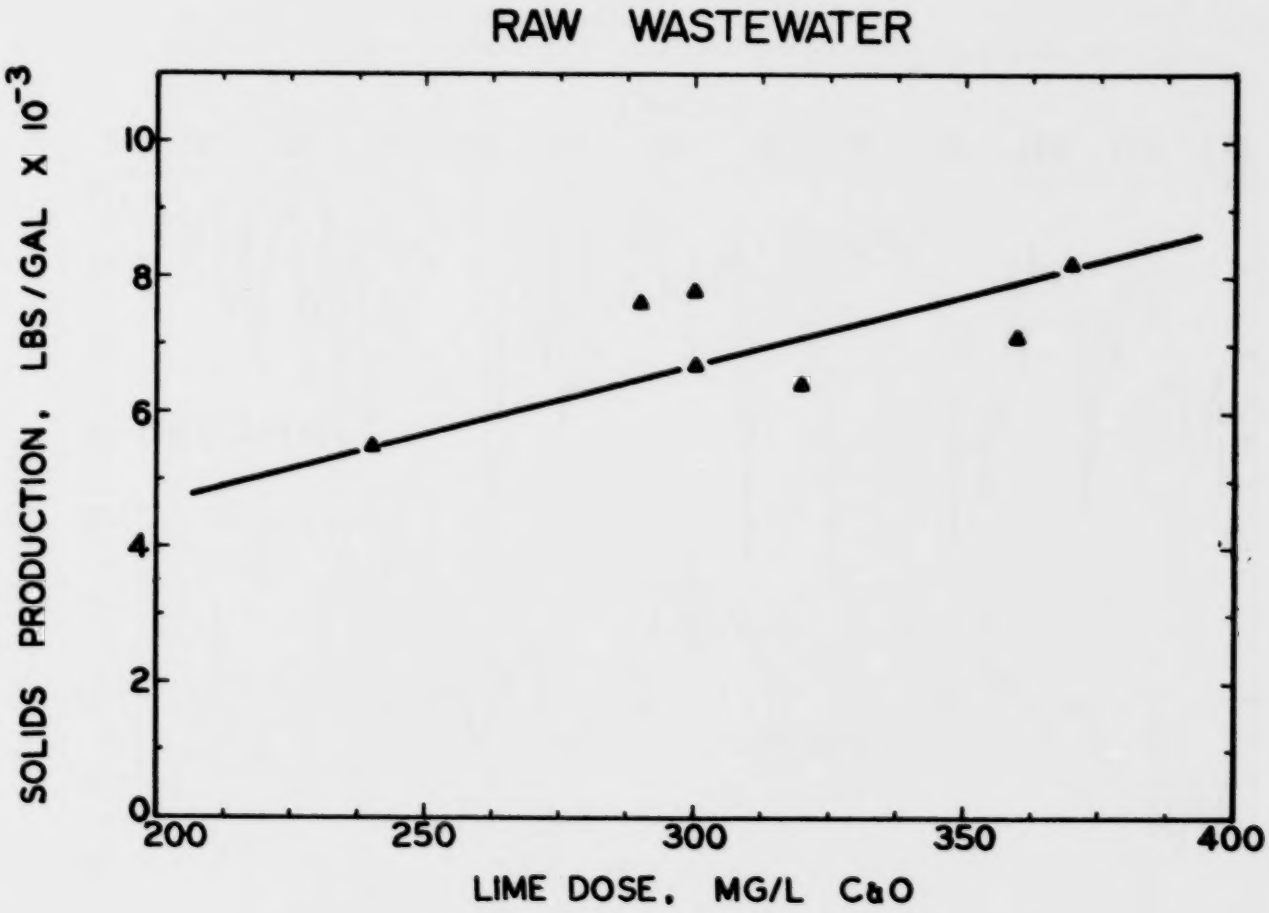

FIGURE 7 - Solids Production and Lime Addition

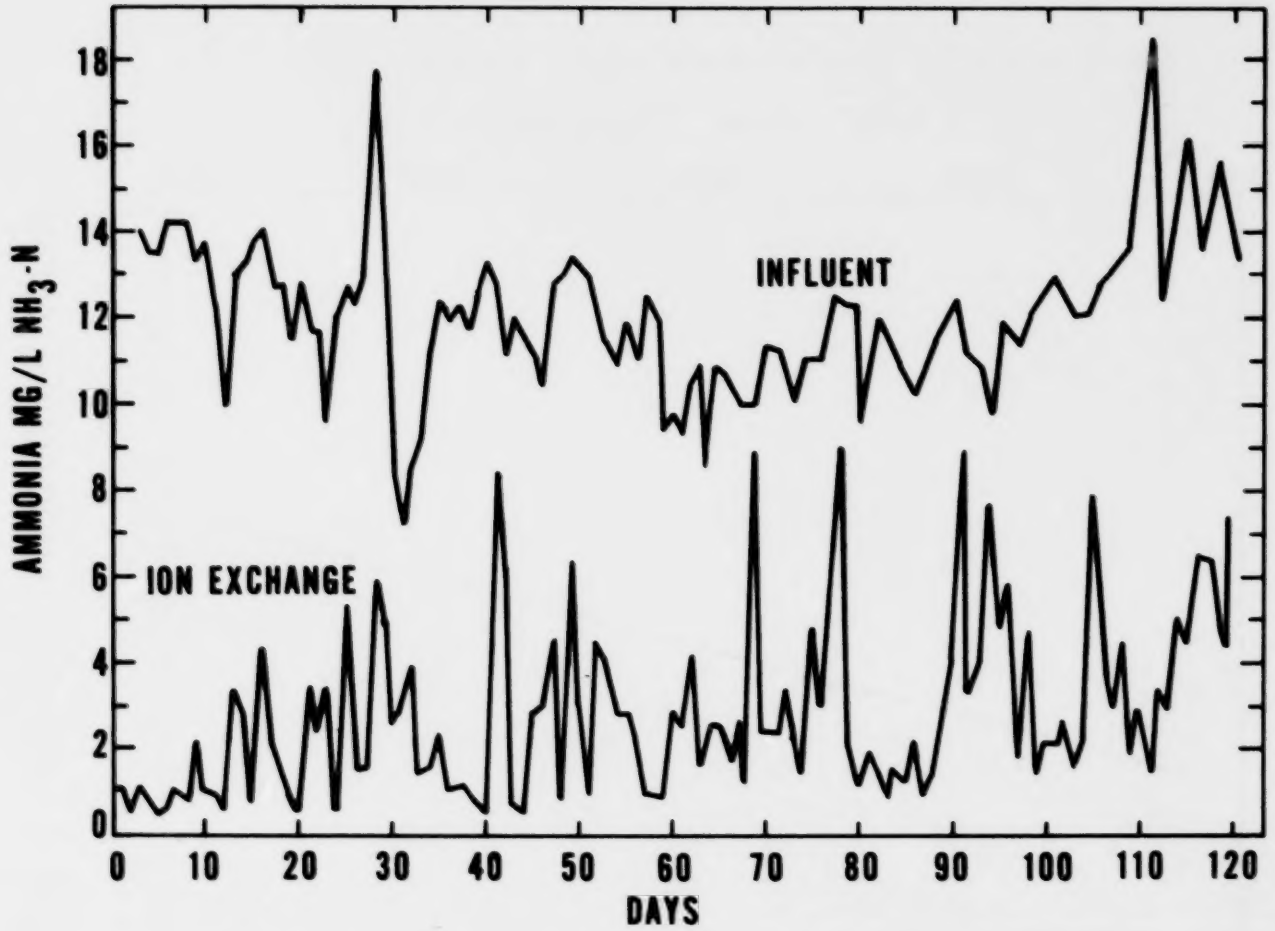

FIGURE 8 - Ammonia Removal in Selective Ion Exchange with Four Hour Operator Surveillance

TABLE 3

SELECTIVE ION EXCHANGE[1] AND RESIDUAL POLLUTANTS

	COD mg./l.		TOTAL P mg./l.		SUSPENDED SOLIDS mg./l.	
	IN	OUT	IN	OUT	IN	OUT
March	53	42	.45	.51	3.8	7.1
April	54	41	.27	.16	12	6.4
May	44	38	.18	.16	5.5	21.0
June	42	38	.18	.10	3.4	5.1
July	30	26	.13	.08	5.0	9.0
August[2]	16	19	.10	.09	6.8	7.0
September[2]	13	23	.11	.11	3.0	3.6
December[2]	20	17	.09	.08	6.7	24.4

1 Ion exchange was operated intermittently

2 Ion exchange placed after carbon adsorption.

of the regenerant and service cycle streams, a major contributor to the poor removal.

Ammonia removals from the D.C. lime clarified raw wastewater, however, (2-hour grab samples) averaged 95% during periods of good operation with 24-hour surveillance (Figure 9). The results on the seventh day in Figure 9 were excluded from the calculation of the average ammonia removal because of incomplete regeneration of the replacement column. In the period of efficient operation, the average run lasted 30 hours before regenerating the lead column.

The most important variable for controlling the process was the pH during regeneration. With a low pH (less than 10.5), not all of the ammonia was removed from the bed and made available for air stripping. A high regenerant pH (greater than 12.0) left deposits of lime on the zeolite, which later during a service cycle, raised the pH of the feed and converted NH_4^+ to unionized NH_4OH. The pH monitoring of lime solutions required frequent checks of the pH electrodes to prevent their scaling. Thus the majority of the daily operational problems were caused by a malfunctioning pH meter and lime scaling difficulties.

During the first five months of operation, the water contained approximately 18.1 mg/l of BOD and 45 mg/l of COD, with potential for biological growth on the zeolite. The pressure drop across the bed increased on every run and the flow had to be reversed for one minute at least twice a run. The high differential pressure, however, was not cumulative from run to run as the high pH regeneration minimized growth. Approximately 0.16 pounds of NaOH and 0.5 pounds of CaO were employed in the regenerant brine for each thousand gallons of water treated.

When ion exchange was placed after carbon adsorption, influent BOD averaged only 5.8 mg/l; the COD, 16 mg/l. Microscopic examination of the regenerant solution, however, showed evidence of biological growth in the columns. The growth did not increase the pressure drop through the bed. The biological growths, apparently leaking from the adsorption system, fouled the exchange minerals and increased the 12 hours regeneration time by about 20%. During the early part of regeneration cycles, larger quantities of lime (approximately a 10% increase) were also unexpectedly needed to maintain the regenerant solution at pH 11.0. The ammonia removal capabilities of the zeolite were not affected.

After 90 days of operation, the stripping tower packing was plugged with calcium carbonate scale and lime. The lime scale was soft and easily removed. The calcium carbonate scale was hard and had to be removed by agitating the packing in water. The lime found in the stripping tower was caused by the erratic operation of the pH controller. The pH control problem was also responsible for the large quantities of backwash water (3-6% of total service flow) required after each regeneration.

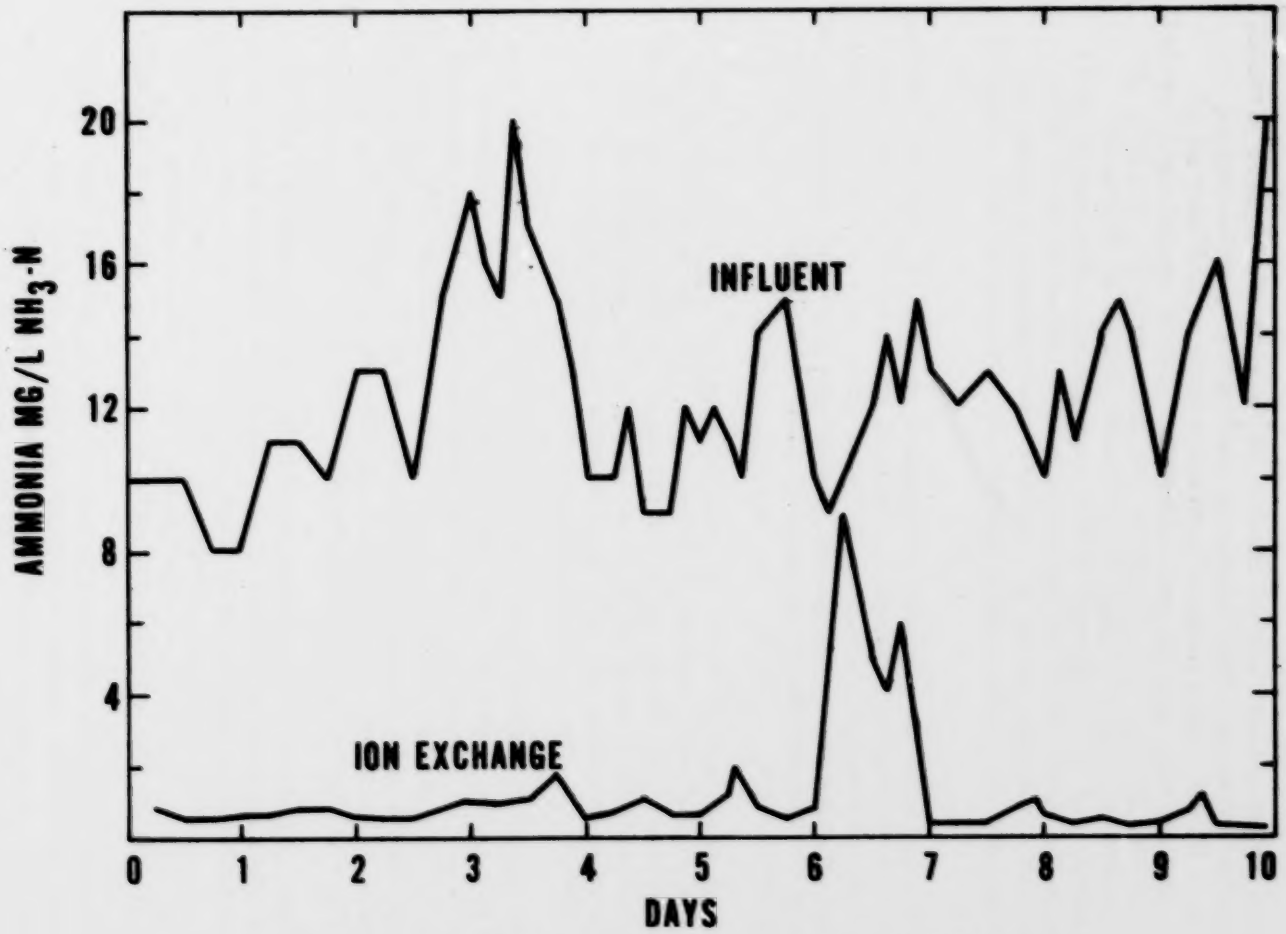

FIGURE 9 - Ammonia Removal in Ion Exchange with Continuous Operator Surveillance

Breakpoint Chlorination Operation

Breakpoint chlorination removed chiefly NH_4^+-N with the organic nitrogen and dissolved organics (TOC) generally unaffected by chlorination (Table 4). In the first month of operation with an influent pH of 9 to 10, the process control was difficult. The pH periodically cycled usually between 6-8 but occasionally the cycle exceeded the 6-8, pH range. Moderately high ammonia breakthrough (Table 4) averaging approximately 0.9 mg/l occurred during this period. The oxidation of ammonia in the first month of operation also produced slightly more nitrate with an average value of 0.8 mg/l than subsequent operation. In earlier work (14) high nitrate production occurred at high reaction pH.

The breakpoint with the influent wastewater pH at 9-10, however, reduced the base (NaOH) used to neutralize the acid produced by chlorination from the stoichiometric (equation 9) requirement of 1.5 pounds of NaOH per pound of chlorine to 0.9 pounds of NaOH per pound of chlorine. The alkalinity in the wastewater at pH 9-10 neutralized some of the acid from the breakpoint.

In the next three months with CO_2 preadjustment of the pH to 7, the controller consistently maintained the pH at 7.0. With effective pH reaction control, the daily NH_4^+-N variation in the effluent (Figure 10) revealed consistently good NH_4^+-N removal. The average influent and effluent concentrations for this period were 11 mg/l and 0.4 mg/l of NH_4^+-N. The NO_3^- in the effluent averaged 0.6 mg/l as N.

The NH_4^+-N removals represented a significant improvement over the first month's operation. However, the NaOH usage increased to 1.8 pounds per pound of chlorine (Table 4). The increased base requirement occurred because the CO_2 converted the OH^- alkalinity at pH 10 to HCO_3^- alkalinity which was unavailable for neutralizing acid at pH 7. Since the stoichiometric base requirement is 1.5 pounds of NaOH per pound of Cl_2, the excess CO_2 also appeared to exert an additional base demand.

During the last stage of operation with chlorine to preadjust the pH and with the system on a diurnal flow, control of the breakpoint process was very difficult. The daily average NH_4^+-N variation in the effluent (Figure 10) however, did not reveal the NH_4^+-N breakthrough since sampling was discontinued with loss of breakpoint. The monthly average NH_4^+-N concentrations in the influent and effluent were 9.7 mg/l and 0.5 mg/l.

While the use of Cl_2 in pH preadjustment probably reduced base requirements, the base usage during this stage of operation could not accuratedly be determined because of frequent loss of breakpoint. Thus an improved control system was needed to operate the split chlorine treatment approach and to handle the diurnal cycle.

TABLE 4

Breakpoint Chlorination
of
Lime Clarified and Filtered Raw Wastewater

Month	April	May	June	July	August
Flow, gpm	25	25	25	25	22.5-55.5
Influent					
pH	9.9	9.3	9.3	9.2	9.0
P. alk, mg/l	70	45	54	31	30
M.O., alk., mg/l	140	84	96	82	80
NH_4^+-N, mg/l	12.6	11.6	10.8	10.4	9.7
TKN-N, mg/l	14.2	14.1	12.2	11.9	10.7
NO_3^--N, mg/l	0.16	0.02	0.0	0.0	0.0
TOC, mg/l	22.6	19.9	16.7	17.0	18.3
pH Adjustment	None	CO_2	CO_2	CO_2	Cl_2
pH after Adj.	9.9	7.0	7.0	7.0	7.0
Reaction Conditions					
pH	7.0	7.1	7.2	7.3	---[1]
Cl:N, lb/lb.	9:1	9:1	9:1	9:1	9:1
NaOH:Cl, lb/lb.	0.9	1.8	1.8	1.8	---[1]
Effluent					
M.O., alk., mg/l	52	100	124	118	60
NH_4^+-N, mg/l	0.9	0.4	0.4	0.4	0.5
TKN, mg/l	4.8	2.5	2.0	1.8	2.1[1]
NO_3^--N, mg/l	0.8	0.7	0.6	0.5	0.5
TOC, mg/l	23.1	20.1	18.8	18.8	16.9

[1] pH cycled with poor process control; breakpoint was frequently lost. Data represents periods of successful breakpoint; base requirement and pH not accurately determined.

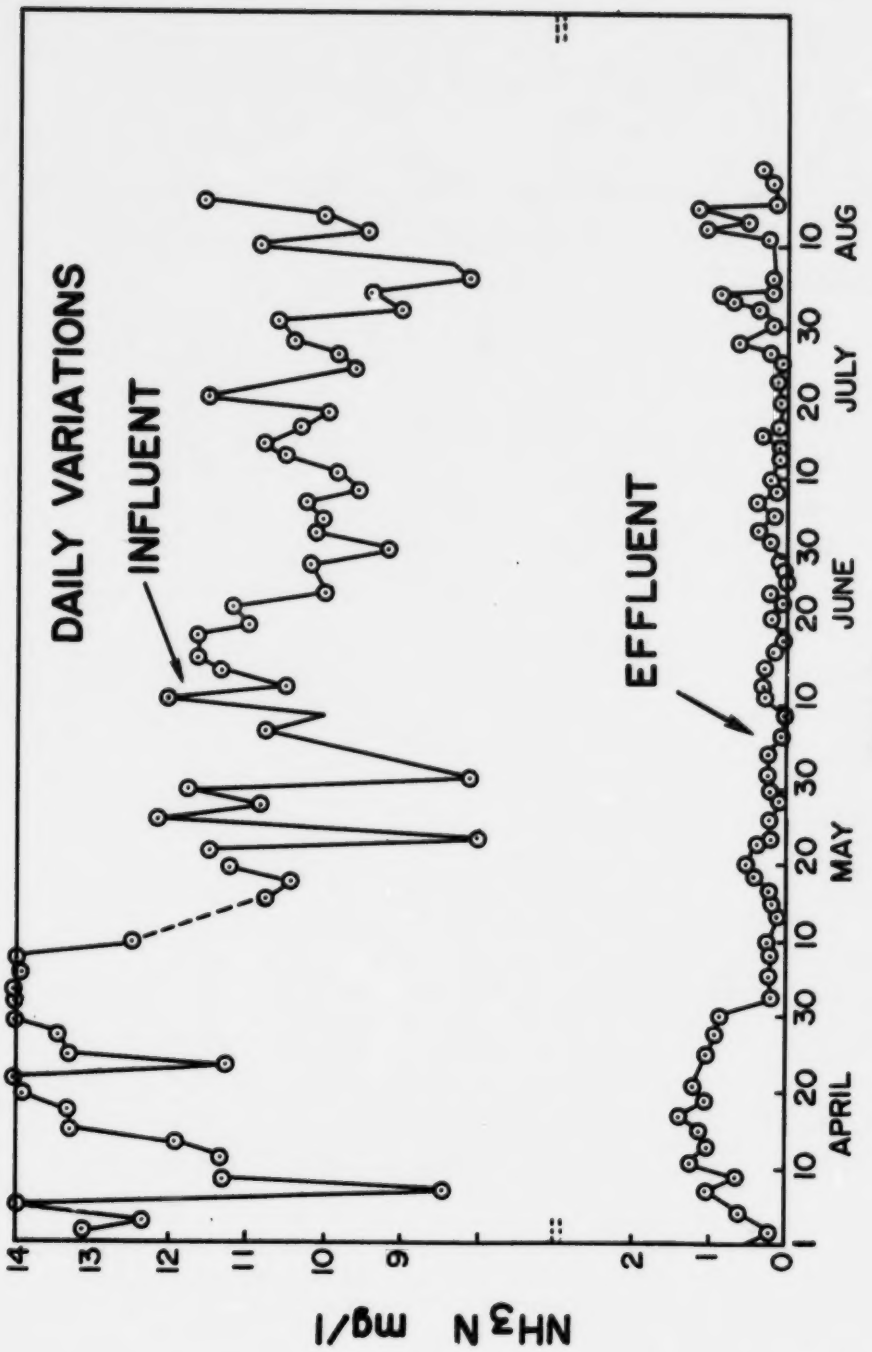

FIGURE 10 - Daily Ammonia Removal in Breakpoint Chlorination

Carbon Adsorption Operation

The carbon adsorption process included two different periods of operation, one without chlorine in the influent wastewater (selective ion exchange or no nitrogen removal) and one with chlorine in the influent wastewater (breakpoint chlorination). In the period without chlorine, the soluble BOD (20 mg/l) in the influent wastewater caused heavy anaerobic biological activity on the carbon columns. This activity produced appreciable H_2S production (2-3 mg/l of H_2S) in the product water and objectionable odors, relatively high pressure losses (25 psig in a 24 hour period) across the lead column and high carbon losses during backwash into the carbon decant tank. Since carbon recycle from the decant tank to the backwashed carbon columns was not employed because of the heavy slimes, carbon losses exceeded 25% between the carbon replacement cycles.

Normally the lead carbon column was backwashed once a day by the following procedure:

1. *10 minutes of backwash at 2 gpm/ft^2.*
2. *10 minutes of backwash at approximately a 17% bed expansion (10-11 gpm/ft^2) with a simultaneous surface wash at 3 gpm/ft^2.*
3. *10 minutes of backwash at 29% bed expansion (13-16 gpm/ft^2 as a function of water temperature).*

Each of the remaining three columns were backwashed by the above procedure once a week. Beginning in July 1970, a modification in the backwash procedure was evaluated for controlling the biological activity on the carbon columns. In July, after the replacement of the first half of the carbon (2 columns) with virgin carbon, the backwash water during the period (10 minutes) with surface wash contained on alternate days 300 mg/l of NaOH in an attempt to control the biological activity in the lead column. The remaining columns were backwashed once a week with the sodium hydroxide added during the surface wash period.

The backwash with sodium hydroxide was continued until the end of October 1970 and produced a pH of 9 in the backwash effluent. The use of the high pH backwash water, however, did not reduce the pressure drop (25 psig per day) across the lead column, and did not control the H_2S production (2.4 mg/l of H_2S in a September 1970 test). The plant operation exhibited high backwash carbon losses of about 13% between carbon replacement cycles.

In November 1970 after a second carbon replacement cycle, the NaOH in the backwash water was increased to 600 mg/l in the surface wash period and the time of backwash surface wash increased from 10 minutes to 30 minutes. The pH in the effluent washwater increased from 9 with the 300 mg/l dose to 11.3 with the 600 mg/l dose. Unfortunately, the wastewater temperature began to decrease significantly and the evaluation

of the very high backwash sequence for controlling biological activity was complicated by the decreasing temperature. While the amount of H_2S and the plant's odor problems decreased, the pressure drop in the lead carbon column remained high. In late December 1970, a support plate in the lead carbon column ruptured and accurate carbon losses could not be evaluated. In addition, with the replacement of carbon in November, the residual organics in the carbon effluent did not exhibit as large a decrease in concentration as expected. After only fourteen days of operation with the new carbon charge, the TOC and COD unexpectedly rapidly increased. While the increase occurred with an accompanying increase in influent COD, the residual was considerably higher than that obtained for similar carbon loading in previous operation. The low removal continued through December 1970. The decrease in organic removal appeared to have been caused by a combination of an increase in influent organics, a decrease in water temperature, and a fouling (or scaling by $CaCO_3$) of the carbon with the high pH backwash water.

While recognizing that the backwash system on the carbon columns was not ideal and could be improved by redesign, the results of the biological activity (H_2S, slime, etc.) indicated a problem within physical-chemical treatment of raw wastewater that must be considered in the system design. The carbon columns may have to be converted to upflow expanded beds to eliminate or reduce the need for backwashing or employ a suitable technique such as breakpoint chlorination ahead of adsorption to control the biological activity.

In the second period of operation, breakpoint chlorination ahead of the adsorption system supplied combined and free chlorine (1-10 mg/l) in the influent to the carbon column. The presence of the chlorine minimized biological activity and controlled but did not completely eliminate H_2S odors. Sufficient anaerobic activity persisted in the carbon columns to denitrify the small (0.6 mg/l) amount of nitrate produced by the breakpoint process. Essentially complete dechlorination required approximately three quarters of the detention time of the carbon columns.

The pressure drop in the carbon columns with the chlorinated influent did not exceed 10 psig in 48 hours and backwashing of the lead column was performed once every 48 hours. The previous high carbon losses and the heavy biological growth did not occur and the adsorption column operation behaved similarly to that of earlier carbon studies on tertiary physical-chemical treatment.

Without chlorine in the influent water, the organic residuals (TOC and COD) in the carbon column effluent revealed a repeating pattern in which low residuals (Tables 5 and 6), (approximately 8 mg/l of COD and 3 mg/l of TOC in the first month of the first replacement cycle) occurred during initial operation with virgin carbon and then gradually increased (22 mg/l of COD and 8 mg/l of TOC in the last month of the first replacement cycle) before the replacement of one half of the carbon (Figures 11 and 12). A similar pattern occurred in the second

TABLE 5

COD REMOVALS IN PHYSICAL CHEMICAL TREATMENT
OF
RAW WASTEWATER

Month	Raw	Clarified		Filtered		Nitrogen Rem.[1]		Adsorbed	
	mg/l	mg/l	%Rem	mg/l	%Rem	mg/l	%Rem	mg/l	%Rem
March 70	347	66.2	81	53.9	84	41.3	88	8.2	98
April 70	311	56.8	80	51.8	82	39.2	85	12.7	96
May 70	299	52.5	83	45.2	85	38.4	87	16.4	95
June 70	302	48.5	84	44.9	85	48.2	88	18.7	94
July 70	282	40.4	86	36.1	87	25.6	91	7.8	97
Aug. 70	289	43.6	85	45.1	84	22.9[2]	92	15.4	94
Sept. 70	261	59.1	77	48.6	81	23.0	91	16.5	94
Oct. 70	351	58.1	84	55.0	84	----	--	22.2	94
Nov. 70	323	57.6	82	50.2	85	----	--	17.1	95
Dec. 70	308	63.9	79	55.6	82	16.8[2]	95	20.3	93
Feb. 71	282	60.4	78	49.3	82	----	--	24.4	91
March 71	297	63.1	79	57.1	81	----	--	17.1	94
April 71	300	64.7	78	54.9	82	65.1[3]	78	13.6	96
May 71	284	55.2	81	50.5	82	66.1[3]	77	15.2	95
June 71	262	55.2	79	37.8	86	55.1[3]	79	18.8	93
July 71	263	44.2	83	38.6	85	48.2[3]	82	20.5	92
Aug. 71	250	51.5	79	46.1	82	51.9[3]	79	----	--

[1] Ion exchange or breakpoint chlorination or none

[2] Ion exchange relocated after carbon adsorption

[3] Breakpoint chlorination employed in P.C. treatment

Note: Ion exchange process operated intermittently
% Removals are accumulative.

TABLE 6

TOC REMOVAL IN PHYSICAL-CHEMICAL TREATMENT OF RAW WASTEWATER

Month	Raw	Clarified		Filtered		Nitrogen Rem[1]		Adsorbed	
	mg/l	mg/l	% Rem.	mg/l	% Rem.	mg/l	% Rem.	mg/l	% Rem.
Mar. 70	118	25.5	78	20.1	83	14.9	87	3.7	97
Apr. 70	102	22.8	77	19.9	81	14.8	85	4.9	95
May 70	114	18.8	84	16.8	85	13.5	88	8.1	93
June 70	85	18.1	79	18.5	78	14.5	83	8.3	91
July 70	78	17.6	78	17.3	78	11.8	85	5.2	93
Aug. 70	96	17.5	82	18.4	81	7.6[2]	92	6.1	94
Sept. 70	118	23.1	80	22.3	81	7.7[2]	93	8.3	93
Oct. 70	119	24.3	80	22.1	81	--	--	7.5	94
Nov. 70	122	24.0	80	25.7	79	--	--	10.1	92
Dec. 70	112	26.6	76	25.2	78	9.5[2]	92	10.1	91
Feb. 71	96	21.6	78	21.6	78	--	--	12.1	87
Mar. 71	106	24.8	77	22.8	79	--	--	9.1	91
Apr. 71	94	24.5	74	22.6	76	23.1[3]	75	6.2	93
May 71	92	22.5	76	19.9	78	20.1[3]	78	7.4	92
June 71	95	20.7	78	16.7	82	18.8[3]	80	8.9	91
July 71	86	19.6	77	17.0	80	18.8[3]	78	10.1	88
Aug. 71	72	20.4	72	18.3	75	16.9[3]	77	--	--

1 Ion exchange or breakpoint chlorination or none

2 Ion exchange relocated after carbon adsorption

3 Breakpoint chlorination employed in P.C. treatment

Note: Ion exchange process operated intermittently
% Removals are accumulative

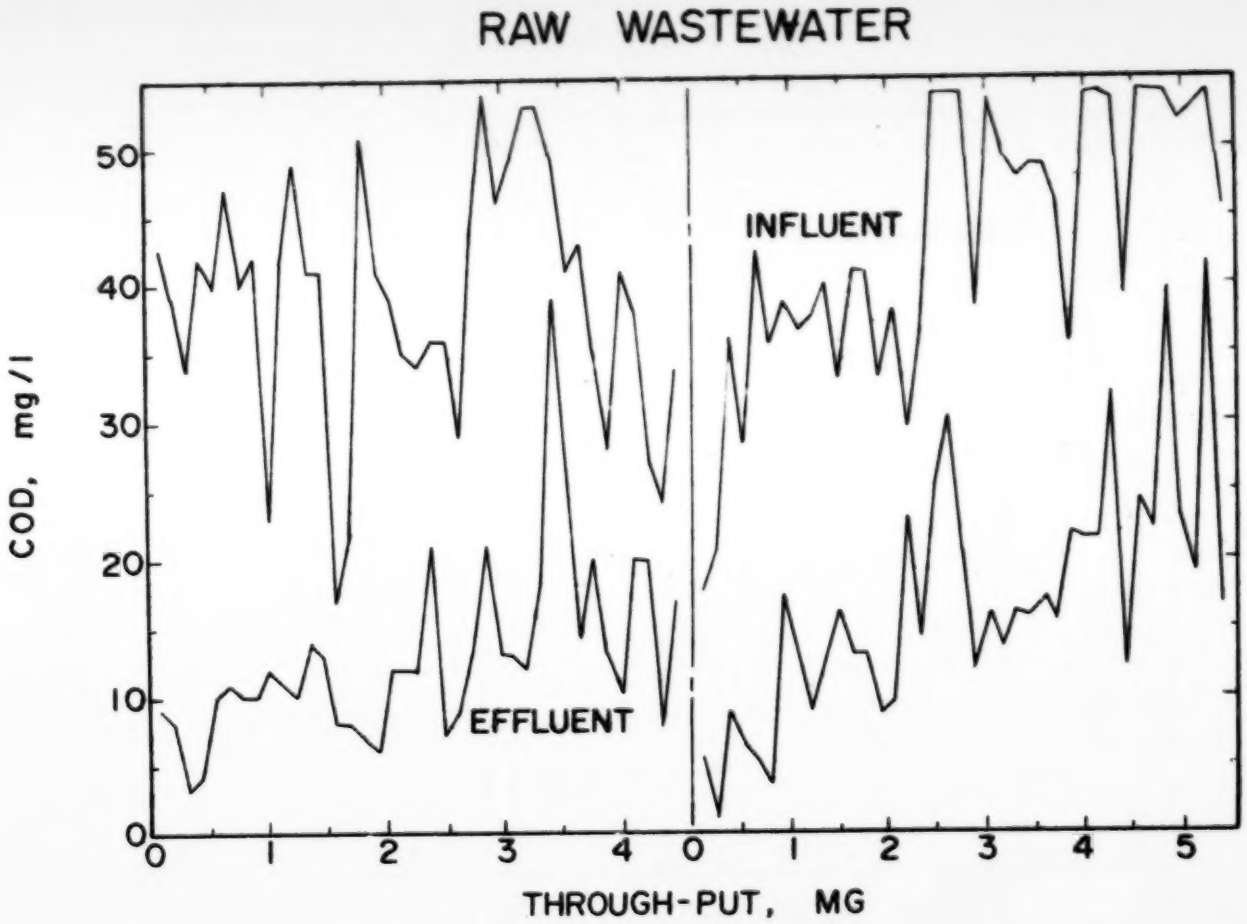

FIGURE 11 - Daily Removal of COD in Carbon Adsorption

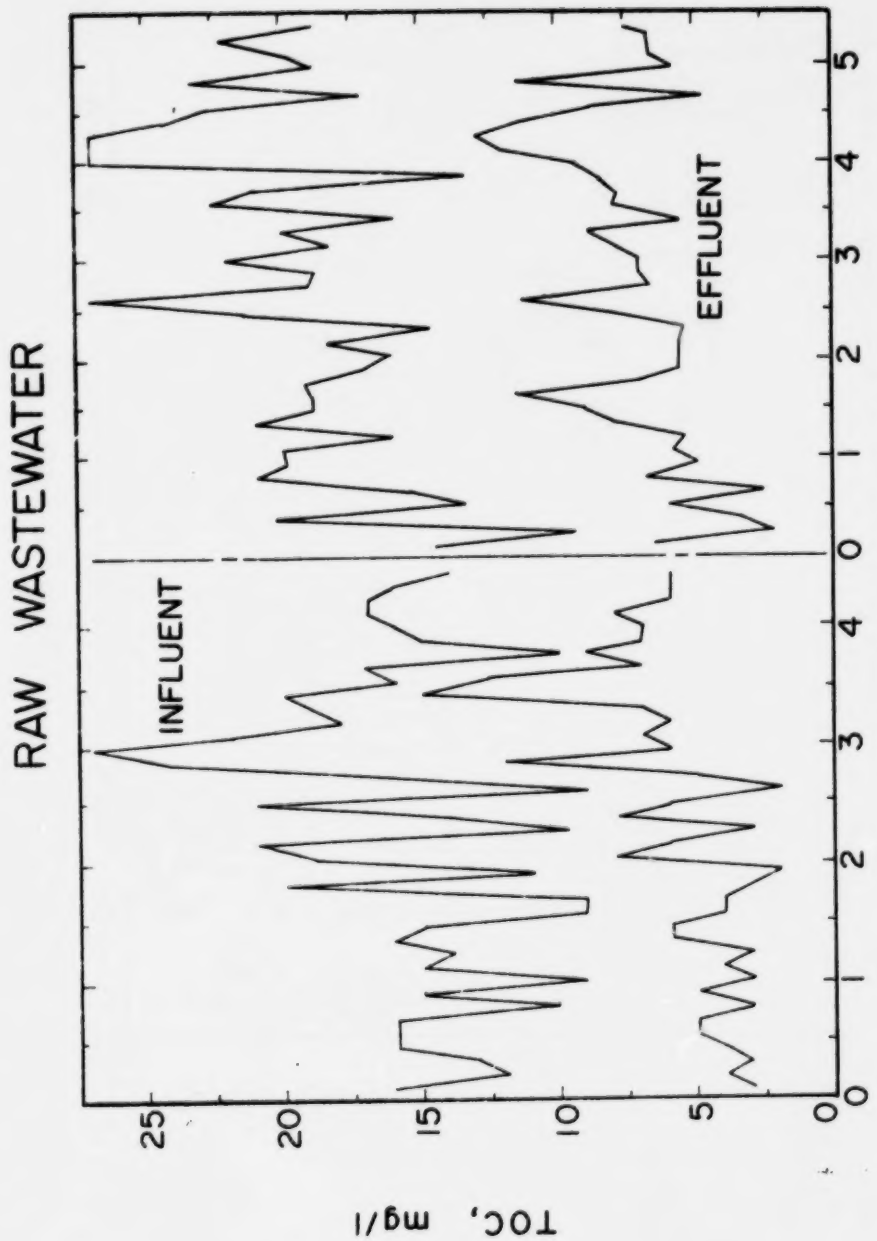

FIGURE 12 - Daily Removal of TOC in Carbon Adsorption

carbon replacement cycle.

During the use of the very high pH backwash procedure (600 mg/l NaOH) in the third replacement cycle, however, the adsorption process did not exhibit the normal removal pattern. The residual COD and TOC in the first month of operation (November 1970) after the second carbon replacement were unusually high and averaged 17 and 10 mg/l, respectively. With the discontinuance of the high pH backwash in December 1970, the average residual COD and TOC of 17 and 9 in the last month (March 1970) before the third carbon replacement were the same as in November and thus indicated that the suspected fouling ($CaCO_3$ scale) did not remain on the carbon.

The presence of chlorine in the influent to the adsorption process did not alter the basic pattern of increasing organic residuals in the effluent with increasing carbon loading. The average COD and TOC residuals (Tables 5 and 6) increased, respectively, from 13.6 mg/l and 6.2 mg/l in the first month (April) with chlorination and after the third carbon replacement to 20.5 mg/l and 10.1 mg/l in the last month (July 1971) of the carbon study.

The adsorption process with a normal average column hydraulic loading of 7 gpm/ft^2 exhibited organic loadings as described in Figure 13 and Table 7. In the operation without chlorine in the influent, the organic loadings increased with increasing biological activity on the carbon columns from 0.13 lb of TOC/lb of carbon (0.4 lb of COD/lb of carbon) at the first replacement to 0.30 lb TOC/lb of carbon (0.74 and 0.70 lb of COD/lb of carbon) for the next two replacements. With chlorine in the influent, the carbon loading was 0.25 lb of TOC/lb of carbon at the end of the study. Further work is needed to determine whether the reduced biological activity with breakpoint chlorination will produce a substantial decrease in the activated carbon loading.

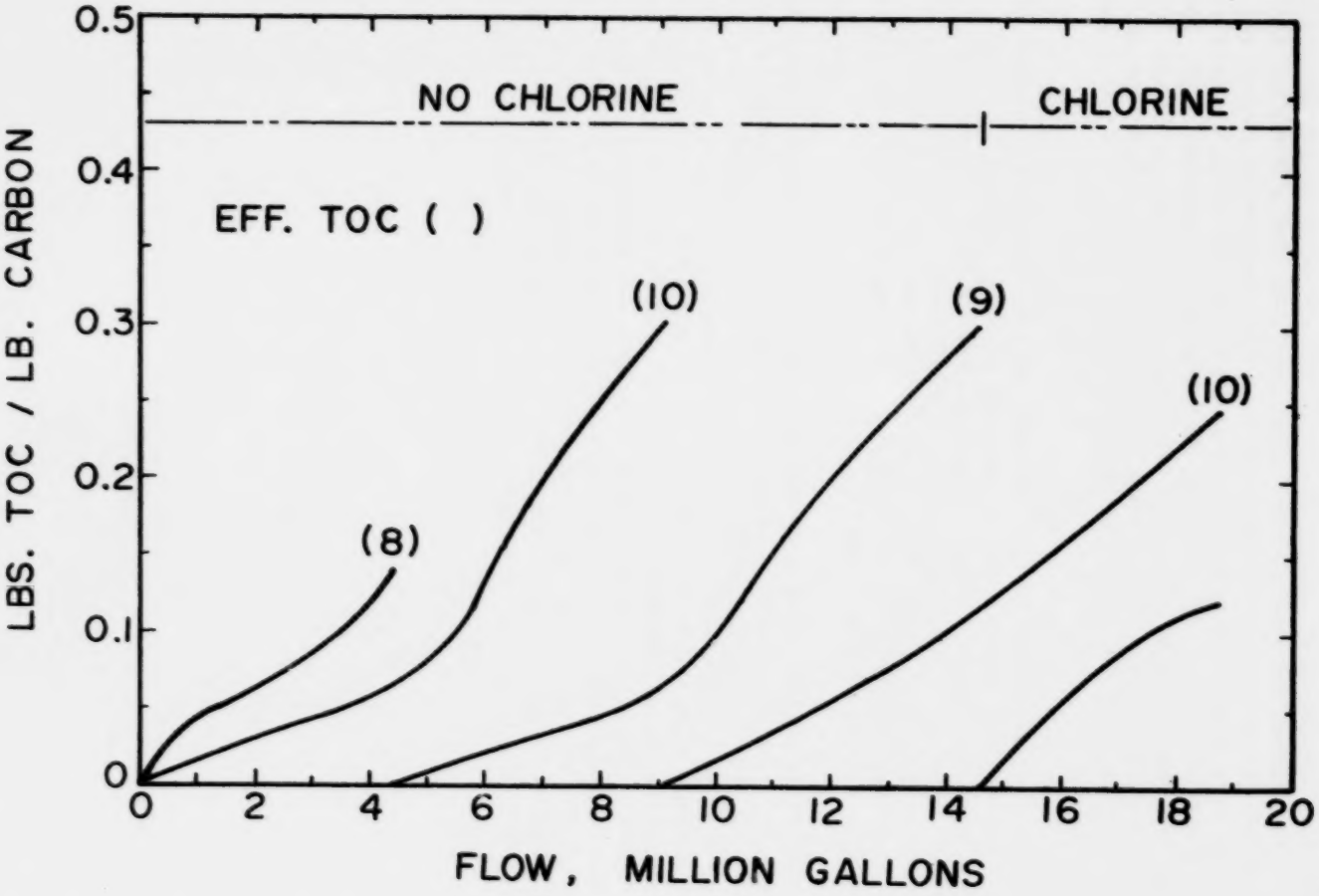

FIGURE 13 TOC Loading on Activated Carbon

TABLE 7

ORGANIC LOADINGS ON ACTIVATED CARBON

Date	Operation	Flow[2] MG	First Stage[1] lb COD / lb Carbon	First Stage[1] lb TOC / lb Carbon	Second Stage lb COD / lb Carbon	Second Stage lb TOC / lb Carbon
3-10-70	Startup	0	-	-	-	-
6-28-70	Replacement	4.2	0.41	0.13	0.15	0.066
10-26-70	Replacement	9.2	0.74	0.30	0.16	0.063
3-16-71	Replacement	14.6	0.70	0.30	0.34	0.17
7-30-71	End	18.8	-[3]	0.25	-[3]	0.12

[1] First stage included first 2 carbon columns
Second stage included last 2 carbon columns

[2] The flow is the accumulated flow in millions of gallons

[3] Residual chlorine in the breakpoint process prevented accurate measurement of COD

SECTION VI

OVERALL PERFORMANCE OF PHYSICAL-CHEMICAL TREATMENT

Organics and Solids Removal

Lime clarification removed approximately 80% of the organics (TOC, BOD, and COD) from the wastewater (Tables 5, 6, & 8). Filtration increased these removals only slightly (1-4%) producing water containing 15-20% of the original organics. Ion exchange then removed from 15 to 35% of these residual ("soluble") organics, increasing the accumulated organic removals to more than 85%. Breakpoint chlorination, however, when substituted for the ion exchange did not increase the accumulated organics removal.

With virgin carbon, the adsorption system in the first month removed 75% of the TOC, 78% of the BOD, and 80% of the COD entering the columns with average residuals of 3.7 mg/l of BOD and TOC and 8.2 mg/l of COD. Adsorption increased the overall organic removals to 97-98%.

During typical operation with high organic loading and normal biological growth on the activated carbon in the fourth month, the carbon removed 55% of the influent (soluble) TOC, 22% of the BOD_5, and 56% of the COD with average residuals of approximately 8 mg/l for BOD_5 and TOC and 19 mg/l for COD. The overall organic removals through the plant decreased to between 91 and 94%. The spent carbon (the first half of the carbon) was then replaced at the end of the fourth month (June 1970).

The replacement of the spent carbon with virgin carbon reduced the organic residuals for the fifth month (July 1970) to approximately the same level as those experienced during the first month of operation (March 1970). As the organic loading on the carbon increased, the pattern of decreasing overall organics removal efficiencies was again noted. The relocation of the ion-exchange process in August to a position following the carbon adsorption process did not significantly increase the removal of organics from the adsorption column effluent nor alter the overall removal efficiencies.

Substitution of breakpoint chlorination for ion exchange also did not alter the basic overall organic removal pattern although the final effluent BOD from adsorption with prior chlorination for nitrogen removal was slightly lower than earlier operation and averaged about 5 mg/l. For the entire operation, the physical-chemical plant removed approximately 95% of the COD, 92% of the TOC and 96% of the BOD with average residuals of 16 mg/l of COD, 8 mg/l of TOC, and 6 mg/l of BOD. Laboratory ozonation (29 of the effluent from the carbon columns with 50 mg/l of O_3 reduced the COD to 4 mg/l, the TOC to 4 mg/l and the BOD to zero.

As with organic removal, lime clarification produced consistently good solids removal. During the study, lime clarification produced an average

TABLE 8

BOD REMOVAL IN PHYSICAL-CHEMICAL TREATMENT
OF
RAW WASTEWATER

Month	Raw	Clarified		Filtered		Nitrogen Rem[1]		Adsorbed	
	mg/l	mg/l	% Rem.	mg/l	% Rem.	mg/l	% Rem.	mg/l	% Rem.
Mar. 70	142	31.4	78	23.7	83	16.7	87	3.7	98
Apr. 70	126	28.3	78	24.3	81	18.6	85	6.4	95
May 70	158	26.1	83	19.4	88	12.6	92	6.5	96
June 70	111	18.1	84	15.1	86	9.6	91	7.5	93
July 70	99	13.0	86	11.8	88	7.8	92	3.0	97
Aug. 70	98	16.2	83	13.8	86	4.3[2]	95	4.7	96
Sept. 70	115	19.8	83	20.6	82	4.0	97	6.3	95
Oct. 70	131	28.5	78	21.6	84	--	--	7.4	94
Nov. 70	141	29.7	80	23.9	83	--	--	8.3	94
Dec. 70	166	31.9	81	29.3	82	4.4	98	8.1	93
Feb. 71	134	32.3	76	22.7	84	--	--	8.0	94
Mar. 71	152	28.6	81	--	--	--	--	5.8	96
Apr. 71	165.3	36.4	78	21.2	87	--	--	4.6	97
May 71	152.4	28.1	82	--	--	--	--	4.6	97
June 71	129	19.3	85	--	--	--	--	4.7	97
July 71	131	20.7	84	--	--	--	--	7.6	94
Aug. 71	123	20.1	83	--	--	--	--	--	--

1 Ion exchange or breakpoint chlorination or none

2 Ion exchange relocated after carbon adsorption

3 Breakpoint chlorination employed in P. C. treatment

Note: Ion exchange process operated intermittently
% Removals are accumulative

suspended solids removal of 88% as shown in Table 9. Filtration increased the removal to 97%. Further decreases in suspended solids did not occur across the remaining plant processes. The overall removals continued to average approximately 97% with about 4 mg/l of residual suspended solids.

Phosphorus Removal

Lime clarification consistently removed 97% of the total phosphorus from the raw wastewater. In March of 1970, lime clarification reduced the total phosphorus (Table 10) to 0.45 mg/l as P. Treatment through adsorption further reduced the total phosphorus to 0.21 mg/l (98% removal). As the water temperature increased in the summer, the total phosphorus residuals gradually decreased to 0.17 mg/l after clarification, and to 0.08 mg/l after complete treatment. With the onset of colder weather, the phosphorus removal again decreased slightly with residuals of about 0.2 mg/l. For the complete study, physical-chemical treatment removed 98% of the total phosphorus with an average phosphorus residual of 0.14 mg/l.

Nitrogen Removal

The raw wastewater in the District of Columbia contained chiefly organic nitrogen and ammonia with usually less than about 0.07 mg/l of nitrate nitrogen. Lime precipitation removed about 30% of the total nitrogen (TKN and nitrate) from the water (Table 11). The nitrogen removed in clarification was approximately 75% organic (particulate) and 25% (8% of the total original nitrogen) ammonia (Table 12). The small but consistent ammonia removal across the clarification process probably occurred by stripping from the water at high pH into the air.

Filtration increased the total nitrogen removal to about 35%. Ion exchange (clinoptilolite) essentially removed only ammonia from the wastewater. While with careful operator surveillance, the exchange process (Figure 9) reduced the NH_4^+-N to less than 1 mg/l with removals greater than 90%, when unattended the ammonia residuals in the ion exchange effluent increased. For the first five months with the exchange process ahead of adsorption, the clinoptilolite removed approximately 75% of the ammonia entering the process with nitrogen residuals averaging 2.6 mg/l of NH_4^+-N and 2.3 mg/l of other nitrogen (4.9 mg/l of total N, Table 12). Little additional removal of nitrogen occurred in the adsorption process.

In the first five months, the ammonia concentrations in the water from the ion-exchange processes consistently increased after carbon adsorption. The soluble organic nitrogen entering the carbon columns (2.3 mg/l) apparently was partially converted by the biological activity on the carbon to ammonia nitrogen. Thus, for maximum nitrogen removal potential, the exchange process was relocated after carbon adsorption for August, September and December 1970. The exchange process only

TABLE 9

SUSPENDED SOLIDS REMOVAL IN PHYSICAL-CHEMICAL TREATMENT OF RAW WASTEWATER

Month	Raw	Clarified		Filtered		Nitrogen Rem[1]		Adsorbed	
	mg/l	mg/l	%Rem	mg/l	%Rem	mg/l	%Rem	mg/l	%Rem
March 70	180	19.3	89	4.6	98	7.1	96	2.7	99
April 70	160	22.7	86	10.3	94	6.4	96	4.6	97
May 70	164	12	93	5.1	97	21	87	6	97
June 70	159	6.3	96	4.6	97	5.1	97	4.3	97
July 70	144	8.9	94	4.3	97	9	94	4	97
Aug. 70	139	17.5	87	4.2	97	7.0[2]	95	5.9	96
Sept. 70	136	23.5	83	4.2	97	3.6[2]	97	4.9	96
Oct. 70	168	25.5	85	4.7	97	---	--	3.3	98
Nov. 70	173	25.0	85	6.9	96	---	--	4.4	98
Dec. 70	163.4	24.4	85	9.2	94	---[2]	--	5.9	96
Jan. 71									
Feb. 71	147	9	94	2	99	---	--	2.0	99
March 71	156	14.9	90	4.9	97	---	--	2.8	98
April 71	164	13.2	92	4.5	97	4.0[3]	98	3.0	98
May 71	159	22.5	96	4.3	97	7.5[3]	95	3.8	98
June 71	162	34.3	79	4.3	97	2.5[3]	98	3.0	98
July 71	146	21.7	85	5.9	96	3.7[3]	98	3.6	98
Aug. 71	162	32	80	4.9	97	3.3[3]	98	---	--

[1] Ion exchange or breakpoint chlorination or none

[2] Ion exchange relocated after carbon adsorption

[3] Breakpoint chlorination employed in P.C. treatment

Note: Ion exchange process operated intermittently
% Removals are accumulative

TABLE 10

PHOSPHORUS REMOVAL IN PHYSICAL-CHEMICAL TREATMENT
OF
RAW WASTEWATER

Month	Raw	Clarified		Filtered		Nitrogen Rem.[1]		Adsorbed	
	mg/l	mg/l	%Rem	mg/l	%Rem	mg/l	%Rem	mg/l	%Rem
March 70	8.7	0.45	95	0.31	96	----	--	0.21	98
April 70	8.5	0.30	97	0.18	98	0.16	98	0.16	98
May 70	8.9	0.25	97	0.1	98	0.16	98	0.12	99
June 70	8.5	0.16	98	0.14	98	0.10	99	0.14	98
July 70	8.1	0.17	98	0.14	98	0.08	99	0.07	99
Aug. 70	8.0	0.18	98	0.11	99	0.09[2]	99	0.08	99
Sept. 70	8.2	0.25	97	0.16	98	0.11	99	0.09	99
Oct. 70	8.1	0.25	97	0.18	98	----	--	0.11	09
Nov. 70	8.4	0.30	96	0.22	97	----	--	0.11	99
Dec. 70	8.3	0.37	96	0.22	97	0.08[2]	99	0.12	99
Feb. 71	7.5	0.29	96	0.26	97	----	--	0.23	97
March 71	7.6	0.32	95	0.27	96	----	--	0.13	98
April 71	8.1	0.36	96	0.39	96	0.37[3]	96	0.21	97
May 71	7.3	0.30	96	0.23	97	0.32[3]	96	0.23	97
June 71	7.0	0.46	93	0.19	97	0.18[3]	97	0.14	98
July 71	6.9	0.27	96	0.18	97	0.17[3]	97	0.14	98
Aug. 71	6.7	0.30	95	0.23	97	0.16[3]	98	----	--

[1] Ion exchange or breakpoint or none

[2] Ion exchange relocated after carbon adsorption

[3] Breakpoint chlorination employed in P.C. treatment

Note: Ion exchange process operated intermittently
% Removals are accumulative.

TABLE 11

TOTAL NITROGEN REMOVAL IN PHYSICAL-CHEMICAL TREATMENT
OF
RAW WASTEWATER

Month	Raw	Clarified		Filtered		Nitrogen Rem[1]		Adsorbed	
	mg/l	mg/l	% Rem.	mg/l	% Rem.	mg/l	% Rem.	mg/l	% Rem.
Mar. 70	22.9	15.5	32	16.4	28	4.5	80	3.1	87
Apr. 70	21.0	15.6	26	15.8	24	6.0	72	4.2	80
May 70	21.7	15.1	31	--	--	4.3	78	9.7	--
June 70	21.2	14.0	34	13.5	36	4.4	79	8.1	--
July 70	19.8	12.9	35	12.3	38	5.3	73	9.2	--
Aug. 70	20.4	13.5	34	12.9	37	4.7[2]	77	11.9	41.7
Sept. 70	21.9	15.5	24	14.8	32	4.4	80	13.7	37
Oct. 70	23.0	16.1	30	15.5	33	--	--	14.8	36
Nov. 70	22.8	16.0	30	15.9	30	--	--	13.5	41
Dec. 70	23.1	17.3	25	16.9	27	5.0[2]	78	15.2	34
Feb. 71	22.4	14.9	33	14.7	34	--	--	13.4	40
Mar. 71	23.6	16.8	29	15.2	36	--	--	14.3	39
Apr. 71	23.0	15.9	31	14.2	38	5.6[3]	75	4.6	80
May 71	21.4	16.4	23	14.1	34	3.2[3]	85	2.6	88
June 71	20.3	14.0	31	12.2	40	2.6[3]	87	2.5	88
July 71	18.8	13.9	33	11.6	38	2.3[3]	88	2.6	86
Aug. 71	17.9	13.6	24	10.7	40	2.6[3]	85	--	--

1 Ion exchange or breakpoint chorination or none

2 Ion exchange relocated after carbon adsorption

3 Breakpoint Chlorination employed in P.C. treatment

Note: Ion exchange process operated intermittently
% Removals are accumulative

TABLE 12

NITROGEN REMOVAL[1] WITH ION EXCHANGE

Month 1970	Influent		Clarification		Filtration		Ion Exchange		Adsorption		% Removals	
	Total N	NH_3-N	Total N	NH_3-N	Total N	NH_3-N	Total N	NH_3-N	Total N	NH_3-N	Total N	NH_3-N
	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l		
March	23.4	13.7	17.1	12.8	16.1	13.0	4.1	1.7	3.2	3.0	86	78
April	20.7	11.3	15.9	10.9	15.1	10.9	5.8	2.7	4.1	3.8	80	66
May	21.0	12.8	14.8	12.1	13.9	11.7	4.9	2.9	5.2	4.0	75	69
June	20.5	12.7	13.4	11.0	13.1	10.6	4.5	2.6	5.1	3.6	75	72
July	20.6	12.1	13.0	10.4	12.2	10.8	5.3	3.3	4.8	3.6	77	70
Aug.	19.7	12.3	13.1	11.4	11.6	10.9	4.1	3.3[2]	11.2	11.2	79	73
Sept.	21.9	13.3	15.5	13.0	14.8	12.0	4.4	3.1[2]	13.7	12.7	80	77
Dec.	23.1	18.5	17.3	15.1	16.9	13.9	5.0	4.3[2]	15.2	14.1	78	77

1 Data represents only periods of operation with the Ion Exchange system on stream

2 Ion exchange located after adsorption

removed about 75% of the influent ammonia with an average residual of 3.6 mg/l of NH_4^+-N, but the amount of other (organic) nitrogen in the exchange effluent (product water) decreased from an average of 2.3 mg/l to 0.9 mg/l. Thus with careful operator surveillance, the ion-exchange process could have reduced the total nitrogen to approximately 2 mg/l and produced a total nitrogen removal of about 90%. As operated, however, the total nitrogen removal by physical-chemical treatment with the ion exchange averaged 78%.

Total nitrogen removal (Table 11) by physical-chemical treatment without an ammonia removal process (October 1970, November 1970, February 1971, and March 1971) averaged about 39%. The total nitrogen removal after filtration during the same period was about 33%. Thus carbon adsorption increased the accumulated total nitrogen removal by only 6%.

The use of breakpoint chlorination for ammonia removal (Tables 11 and 13) produced an overall total nitrogen removal of about 86% during the study. The average residual total nitrogen of about 2.8 mg/l as N contained approximately 1 mg/l of ammonia nitrogen. Thus a second application of chlorine after carbon adsorption could be employed to reduce the total nitrogen to about 2 mg/l.

TABLE 13

TYPICAL NITROGEN REMOVAL[1] WITH BREAKPOINT CHLORINATION

	TKN-N mg/l	NH_4^+-N mg/l	NO_3^- -N mg/l	NO_2^- -N mg/l	Total N mg/l	Acc. % Rem. of N
Raw	20.3	12.9	0	0	20.3	--
Clarified	14.0	12.3	0	0	14.0	31
Filtered	12.2	10.8	0	0	12.2	40
Breakpoint	2.0	0.4	0.6	0	2.6	87
Carbon	2.5	1.0	0	0	2.5	88

1 June 1970

SECTION VII

ADSORPTION MECHANISM

The results from this work and from earlier work (2) suggest a simple two phase mechanism for the carbon treatment process. Initially the carbon physically adsorbs most of the soluble organics in the wastewater including the highly-soluble poorly-adsorbable but biodegradeable organics in the clarified raw wastewater. The adsorbed organics on the carbon surface are readily available for biological degradation which begins quickly on the carbon columns.

In continuous operation, the developing "fixed film" biological activity removes by biosorption portions of the highly-soluble poorly-adsorbable organics and reduces their breakthrough in the carbon column effluent. The biological growths, however, coat the carbon surfaces and block the pore structure of the carbon granules thus reducing sites for physical adsorption. The heaviest growth occurs at the beginning of the adsorption column and gradually spreads toward the end of the column. Without oxygen added to the wastewater, the biological activity is anaerobic and produces H_2S from the sulfates in the water. The carbon near the end of the column continues to physically adsorb organics from the water but the biological activity releases biological end products and cellular material into the water.

As shown in the earlier work (2), the collodial biological cellular material appears as turbidity in the wastewater and is not readily adsorbed on the downstream carbon granules. The collodial cell material is too small to be filtered by the carbon granules and too big to diffuse into the pores of the carbon. The collodial material and gradually increasing amount of soluble organics appear in the column effluent.

As shown in the current study, the total concentration of organics (BOD, TOC and COD) increases in the effluent with organic loading. Since the biological activity occurs indefinitely, the effluent quality without carbon replacement should eventually deteriorate until the physical adsorptive capacity of the carbon is exhausted or is physically isolated from the aqueous phase through blockage of the pore structure by biological slimes. At this point, the effluent quality should stabilize at a level related to the efficiency of the "fixed film" biological activity. With the biological activity, the carbon loading without replacement can increase indefinitely but this loading really represents biological removal rather than physical-adsorption of organics. Thus the apparent loading as shown in this work, greatly exceeds the typical physical adsorption loading developed from batch carbon isotherm tests (2).

Even with the increased loadings, the desirability of biological activity in the adsorption system has not been determined. While the carbon may accelerate the development of biological activity, especially in the

early operation by providing an adsorbed source of biodegradable organics, the fully developed film may function satisfactorily without the adsorbed organics on the carbon. Indeed if the pores of the carbon becomes clogged with cellular debris, much of the active surface and the adsorbed organics would become unavailable for rapid interaction with the biological film. Study over an extended time of parallel systems, one with a fixed film biological column followed by carbon adsoprtion and the other a carbon column with the biological activity supported on the carbon granules, is needed to evalute any synergistic effects between the physical-adsorption process and the biological process.

If "fixed film" biological activity can be continuously supported on carbon granules, it is likely also to develop on less expensive support media of similar size. Thus a more economical approach may be to gradually develop a fixed film biological reactor on an alternate media and reserve the carbon treatment for chiefly physical-adsorption of the materials leaving the "fixed film" biological column. As the final process in the treatment system, a filtration step with chemical flocculation should be added to remove the collodial cell debris passing through the carbon column and thus improve the final product quality.

These physical-chemical treatment systems, without a process such as chlorination to control biological activity becomes a combination of physical-chemical and biological processes and presents several unknowns in terms of systems reliability. The mechanical handling of large scale "fixed film" columns with heavy biological growth on materials the size of carbon granules with either upflow or downflow operation and the control of the H_2S production without chlorination have not been demonstrated.

In preliminary studies in the EPA-DC pilot plant, the use of oxygen to prevent the H_2S production in the downflow carbon columns produced very heavy growths and caused high pressure losses and excessive backwashing requirements. While more efficient backwashing/surface wash systems *may be developed to minimize growth accumulation and H_2S production, these also require large scale demonstrations.*

SECTION VIII

COSTS

The total estimated water costs (Table 14) for physical-chemical treatment with solids disposal in a 300 MGD plant is 32.6¢ per thousand gallons (30). The costs include recalcination of the calcium carbonate from the second sedimentation stage for lime recovery (approximately 50% recovery).

The cost of approximately 23¢ per thousand gallons for carbon, phosphorus and particulate nitrogen removal were based on processes with known chemical technology and with developed large scale equipment. In contrast, the selective ion exchange costs of approximately 10¢ per thousand gallons required an estimation of the bulk production costs and the life of the clinoptilolite. The ion-exchange process also included that of an untried acid adsorption step to remove the ammonia from the stripping air in the regenerant step. Finally, ion exchange technology has not been employed at the scale of large wastewater treatment plants. Incineration data was not available and estimates of performance were employed.

The estimated cost of breakpoint chlorination (Table 15) for nitrogen removal is 7.32¢ per thousand gallons. The estimate reveals that breakpoint chlorination is a high operating and low capital cost process. The chlorination cost is very sensitive to NH_4^+ concentration increasing very markedly with increasing NH_4^+ concentration. The design criteria used in developing the cost estimates are provided in Table 16.

TABLE 14

PHYSICAL-CHEMICAL TREATMENT COSTS

(Cents per Thousand Gallons)[1]

	Influent Pumping & Grit Removal	Lime Treatment	Filtration	Solids Disposal	Carbon Adsorption	Ion Exchange	TOTALS
FUEL	----	0.5	---	1.2	---	---	1.7
ELECTRICITY	0.1	0.4	---	.1	0.3	0.5	1.4
CHEMICALS	----	2.2	0.3	.1	---	2.6	5.2
SUPPLIES	0.1	0.2	0.1	.1	1.9	1.4	3.8
O & M LABOR	0.4	0.6	0.5	0.9	0.6	0.6	3.6
CAPITAL CHARGES[2]	0.9	4.1	1.0	1.5	4.8	4.6	16.9
Totals	1.5	8.0	1.9	3.9	7.6	9.7	32.6

[1] Plant size 300 MGD based on June 1970 costs

[2] Annual capital cost computed at annual rate of 8% including interest and amortization.

TABLE 15

BREAKPOINT CHLORINATION COSTS[*]
FOR LIME CLARIFIED RAW WASTEWATER

	Cents/1000 gals
Electricity (Mechanical Mixing)	.50
Chemicals[**]	
Chlorine (135 mg/l)	4.22
Lime (1 lb./lb Cl_2)	1.35
Supplies	.05
O & M Labor	.60
Capital charges[***]	.60
Total	7.32

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* Plant size 300 million gal/day, 15 mg/l NH_3-N in, cents/thous. gallons

** Chlorine costs $75/ton; Lime costs $24/ton

*** Annual capital cost computed at annual rate of 8% including interest and amortization.

Cl:N weight ratio 9:1

TABLE 16

DESIGN CRITERIA FOR COST ESTIMATE

GRIT CHAMBERS	
Detention Time (Avg), min.	14.7
LIME TREATMENT	
Rapid Mix Detention Time (Peak), sec.	30
Lime Dose, mg/l	350
Lime Recovery	All of 2nd stage $CaCO_3$
Return Solids as percent of flow	10
Flocculation Detention Time (Peak), min.	10
First Stage Sedimentation Overflow Rate (Peak), gpd/ft^2	1500
Second Stage Sedimentation Overflow Rate (Peak), gpd/ft^2	2000
Sedimentation Detention Time (Avg), hr.	2.5
Recarbonation or Stabilization Detention Time (Peak), min.	10
Ferric Chloride Dose, mg Fe^{+3}/l	4
Lime & Recarbonation Thickeners Feed Rate (Peak), ft^2 day/ton	20
Centrifuge Feed Rate for 36" Dia. Bowl and 8% Feed Solids, dry ton/day	96
Calciner Feed Rate, $\frac{\text{wet ton}}{\text{furnace-day}}$	600
ION EXCHANGE	
Number of Stages in Service	2
Direction of Flow	down

TABLE 16
(CONTINUED)

ION EXCHANGE-Continued	
Type of flow	gravity
Hydraulic Loading (Peak), gpm/ft^2	10
Pressure Drop Across Bed	
1st Stage, lb/in^2	15
2nd Stage, lb/in^2	10
Empty Bed Contact Time per Stage, min.	3.37
Time Each Stage in Service, hr.	24
Time in Regeneration Cycle, hr.	24
Clinoptololite Capacity, gmN/gal	10
Clinoptololite Bulk Density, Dry, lb/ft^3	50
Number of Regeneration Stages	2
Time per Regeneration Stage, hr.	4
Hydraulic Loading for Regeneration, gpm/ft^2	6
Type of Flow for Regeneration	up
Wash Volume after Regeneration, bed volumes	12
Hydraulic Loading for Washing, gpm/ft^2	6
Air-to-Liquid Ratio for Ammonia Stripping, ft^3/gal	200
Hydraulic Loading for Ammonia Stripper, gpm/ft^3	2
Ratio of Ammonia Absorption Spray ($(NH_4)_2 SO_4$ with excess H_2SO_4) to gas, gal/ft^3	1/480
FILTERS	
Hydraulic Loading (Avg), gpm/ft^2	3
Head Loss, ft.	9

TABLE 16
(CONTINUED)

FILTERS-Continued	
Backwash Rate, gpm/ft^2	20
Backwash Time, min/day	10
Surface Wash Rate, gpm/ft^2	3
ACTIVATED CARBON	
Number of Stages	2
Direction of Flow	down
Hydraulic Loading (Avg), gpm/ft^2	3
Empty Bed Contact Time per Stage, min.	20
Pressure Drop per Stage, lb/in^2	10
Carbon Loading, $\frac{mg\ TOC}{gm\ Carbon}$	0.15
Carbon Bulk Density, lb/ft^3	27.5
Carbon Loss per Regeneration, %	5
Backwash Rate, gpm/ft^2	15
Surface Wash Rate, gpm/ft^2	3
Backwash Time, min.	10

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